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Volume I

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Volume I

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ABSTRACT

A general sampling and analytical strategy was developed for use in the identification of potentially hazardous components in process streams and waste streams.

The strategy contains sampling, separation and measurement phases with appropriate options for differing stream types. Sampling utilizes many common techniques and equipment which is generally available. The separation phase relies on liquid-liquid partitioning and various forms of column chromatography. Measurement is accomplished primarily by gas chromatography, gas chromatography-mass spectrometry, spark source mass spectrometry, atomic absorption spectrometry and ion selective electrodes.

This strategy was applied to five selected streams from a petroleum refinery. These streams were: fugitive emissions from atmospheric crude distillation; aqueous condensate from an atmospheric crude still; effluent water from an API Separator; tail gas from a sulfur recovery unit; and, atmospheric emissions from a fluid catalytic cracking regenerator. Background data required to apply the strategy to these streams was acquired using published information on chemical composition and by application of engineering judgment.

Costs were developed for the application of the sampling and analytical strategy using a modular approach. Total costs for the five subject streams depended on options selected, and ranged between 270 and 450 thousand dollars.

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Much of the information used in developing the sampling and analytical strategies and the bases of cost estimates for these strategies was provided by a panel of experts consisting of Dr. William Feairheller of Monsanto Research Corporation, Dayton, Ohio 45407; Dr. Carl Fleagle of TRW Incorporated, TRW Systems Group, One Space Park, Redondo Beach, California 90278; Dr. Peter Jones of Battelle Memorial Institute, 505 King Avenue Columbus, Ohio 43201; Dr. Phillip L. Levins of Arthur D. Little, Acorn Park, Cambridge, Massachusetts 02140; Dr. James H. Smith of Stanford Research Institute, 333 Ravenswood, Menlo Park, California 94025; and Dr. Donald D. Rosebrock of Radian Corporation.

We also wish to acknowledge the valuable assistance provided by consultants through their review of material contained in this report. These contributors included Dr. Phillip W. West at Louisiana State University, Baton Rouge, Louisiana 70803; Dr. David F. S. Natusch at Colorado State University, Ft. Collins. Colorado 80523; Dr. Carter Cook at University of Illinois, Champaign, Illinois 61820; Dr. A. G. Sharkey at the ERDA Pittsburgh Energy Research Center, Pittsburgh, Pennsylvania 15213; Dr. Lawrence Fishbein and Dr. Morris Cranmer at the National Center for Toxicological Research, Jefferson, Arkansas 72079; and Dr. A. Wayne Garrison and Dr. Lawrence Keith at the EPA Southeast Environmental Research Laboratory, Athens, Georgia 30601.

SUMMARY AND CONCLUSIONS

Assessing environmental acceptability of energy conversion plants is difficult because, often, the effluent streams are poorly characterized for their potentially hazardous materials. This problem is particularly apparent for the emerging coal conversion processes because many of them are at the development or pilot plant stages. More information is required about effluents from coal conversion processes in order to assess their environmental impact or to prescribe emission controls.

Basic similarities exist between coal conversion processes and units in a petroleum refinery. The composition of the process streams in the two industries are related and information on refinery processes, stream composition and potentially hazardous compounds in the streams is available in the open literature. Therefore, selected petroleum refinery streams were used to develop an approach for stream characterization that would be applicable to streams in coal conversion units.

The objective of this study was to identify potentially hazardous compounds in refinery streams through a literature survey and to develop a sampling and analytical strategy which would enable measurement of the identified compounds. The strategy was to be general so that it could be applied in other industries with little or no modification. The strategy was to be practical in terms of cost and time requirements. Finally, the strategy was to be based on equipment and techniques readily available to the average laboratory.

The approach for meeting the objective was developed as a concensus of opinion of several contractors and consultants chosen by EPA on the basis of their experience in the field.

Each of these people actively contributed to the approach and costing for this program.

Program Approach

Five refinery streams were chosen to represent the range of difficulty expected to be encountered in sampling and analysis. The five streams were: fugitive emissions from atmospheric crude distillation; aqueous condensate from the atmospheric crude still; effluent water from the API Separator; tail gas from the sulfur recovery unit; and, atmospheric emissions from the fluid catalytic cracking regenerator.

The program was executed in three basic steps. The first step was the process analysis. Information from the literature was collected and processed to obtain the compositions of the selected streams and to characterize the process units associated with the streams. The second step was strategy development. The experience of the contributing contractors was combined to produce a sampling and analytical approach which was then costed.

The first two steps were developed to the extent that the final step - costing - could be reliably estimated. This approach resulted in the development of a philosophy of sampling and analysis rather than a detailed protocol. The philosophy included: what to sample, where to sample, techniques for sampling, techniques for separating the sample, techniques for identifying and quantitating the components, and a discussion of the pros and cons of various options.

Process Analysis

The five process streams were characterized by means of thorough process analysis. The first phase of this work included collecting and classifying chemical data available from the literature. Next, the fates of individual components were considered within the context of the appropriate process conditions. Chemicals were classified as to the potential hazard associated with each. Finally, the physical properties, and where available, the concentrations of chemicals reported to be present in twelve principal refinery streams were summarized.

The process analysis data were used in developing a practical sampling and analytical strategy and for estimating testing costs. Ultimately, this information can be used as an aid in the performance of field tests. The characterizations are not exhaustive with regard to the presence of hazardous components; additional sources of such data are cited in this report. The methodology for collecting and analyzing data is applicable to other types of process plants such as coal conversion and petrochemical units.

Sampling and Analytical Strategy

The sampling and analytical strategy was developed as a series of schemes. A general strategy intended to be applicable to any source was developed first. Specific applications of that strategy were then produced for each of the five refinery streams.

The general strategy was designed to provide optional pathways for sampling, separation, and analysis of material from any source. These sampling, separation, and analytical operations were laid out in flow sheets indicating the sequence of steps from the point of sampling to completion of analysis for a given stream. Costs associated with each step then became the elements from which total estimated costs for sampling and analysis were developed.

Important considerations in selection of these strategies were (1) potential adaptability to other process streams, (2) assurance that the cost per sample was reasonable, and (3) assurance that the technology associated with each step was available and in use today.

Results

A general strategy based on the use of proven technology was developed. The basic approach was to select and use techniques in a "modular assembly" manner such that the strategy could be adapted to essentially any process or effluent stream. Analytical flow sheets showing the sequences in which these modules can be used are presented in the report. Cost estimates were based on analytical elements shown on the flow sheets.

General Strategy. The general sampling and separation strategies are presented in Figures 1.0-1 and 1.0-2. This plan provides a means of assembling well-known procedures in a manner that facilitates analysis of any given stream. The detailed sampling and analytical scheme will be unique for any given stream. However, the sampling and analytical techniques themselves and the procedures for selecting and sequencing them are of general utility.

FIGURE 1.0-1 GENERAL SAMPLING SCHEME

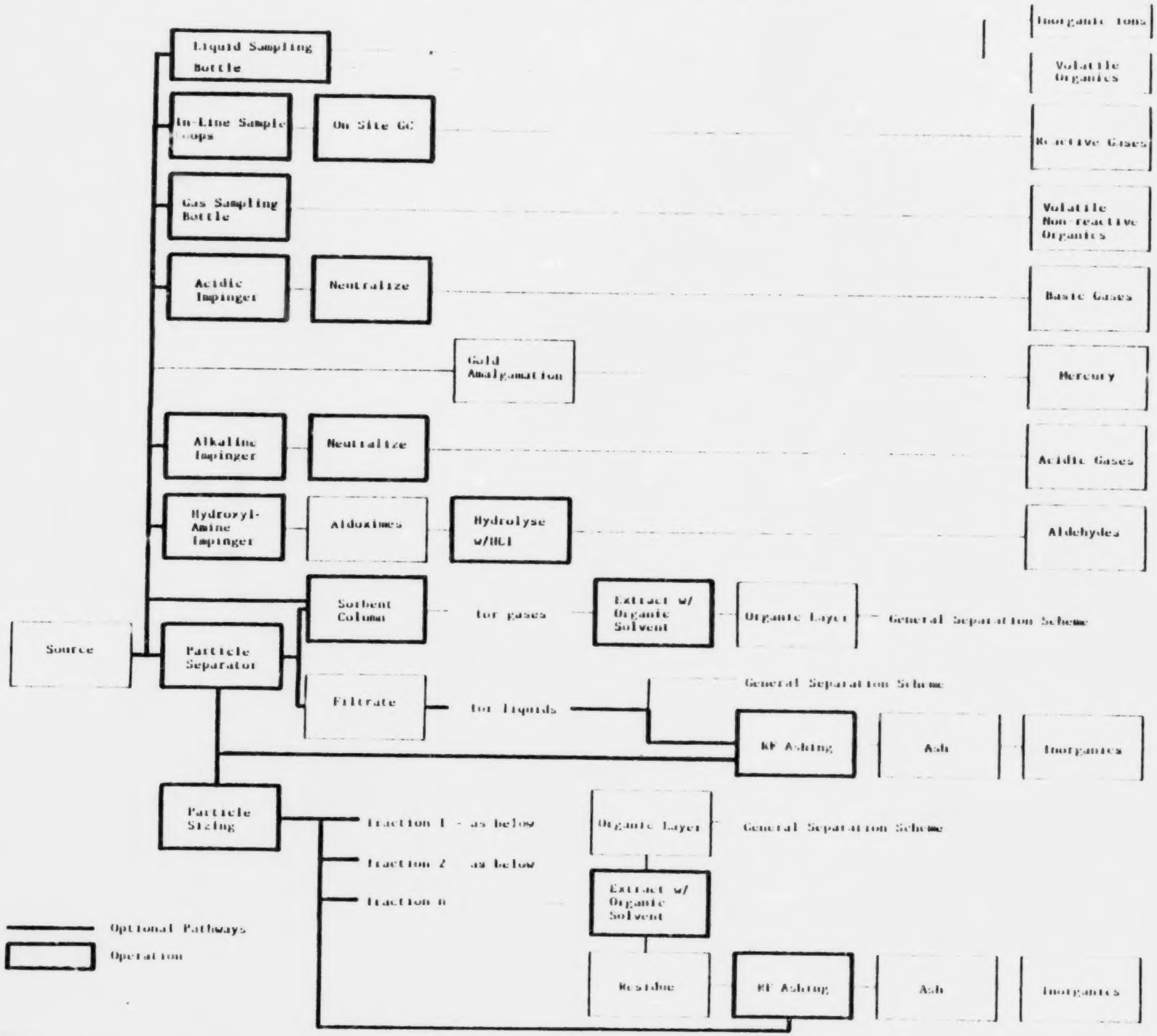
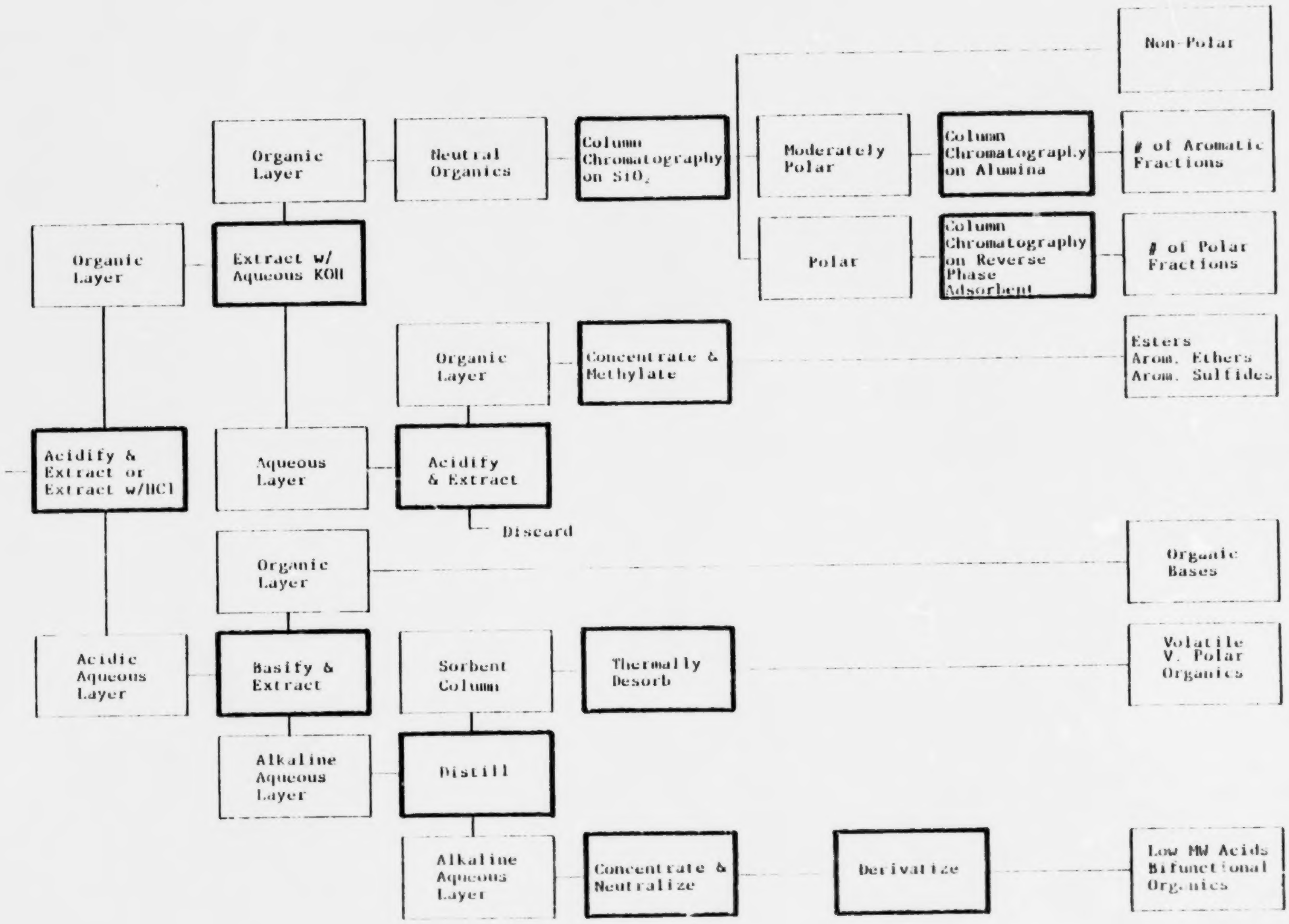

Liquid Sampling Bottle
In-Line Sample Loops
On Site GC
Gas Sampling Bottle
Acidic Impinger
Neutralize
Gold Amalgamation
Alkaline Impinger
Neutralize
Hydroxyl-Amine Impinger
Aldoximes
Hydrolyse w/HCl
Sorbent Column
for gases
Extract w/ Organic Solvent
Organic Layer
General Separation Scheme
Source
Particle Separator
Filtrate
for liquids
General Separation Scheme
RF Ashing
Ash
Inorganics
Particle Sizing
Fraction 1 - as below
Fraction 2 - as below
Fraction n
Organic Layer
General Separation Scheme
Extract w/ Organic Solvent
Residue
RF Ashing
Ash
Inorganics
Inorganic Ions
Volatile Organics
Reactive Gases
Volatile Non-reactive Organics
Basic Gases
Mercury
Acidic Gases
Aldehydes
Optional Pathways
Operation

FIGURE 1.0-2 GENERAL SEPARATION SCHEME


Organic Layer
Acidify & Extract or Extract w/HCl
Acidic Aqueous Layer
Organic Layer
Extract w/ Aqueous KOH
Aqueous Layer
Organic Layer
Basify & Extract
Alkaline Aqueous Layer
Neutral Organics
Organic Layer
Acidify & Extract
Discard
Sorbent Column
Distill
Alkaline Aqueous Layer
Column Chromatography on SiO2
Concentrate & Methylate
Thermally Desorb
Concentrate & Neutralize
Moderately Polar
Polar
Column Chromatography on Alumina
Column Chromatography on Reverse Phase Adsorbent
Derivatize
Non-Polar
# of Aromatic Fractions
# of Polar Fractions
Esters Arom. Ethers Arom. Sulfides
Organic Bases
Volatile V. Polar Organics
Low MW Acids Bifunctional Organics

Provisions were made for conducting programs of varying scope in terms of depth of analysis, the number of streams sampled, and of the number of times similar sources were studied. For this report, these are presented below:

Scope of Analysis

Level I	Screening for the presence or absence of classes or large groups of compounds. This level is generally integrated into Level II where the tests are used to aid in a choice between options.
Level II	Qualitative analyses for specific compounds plus qualitative and semi-quantitative analyses for inorganic materials. This level is used to characterize a sample in terms of what is present and only gives order-of-magnitude approximations of concentration.
Level III	Quantitative analyses of specific elements, ions, and organic compounds or groups of organic compounds. This level provides precise data on concentration. Samples collected for Level II should anticipate Level III. This level generally uses fractions of the sample generated in Level II. Primary difference between Levels II and III is the extent of instrument calibration required.

Definition of Programs

Program A	Sampling and analysis of the five refinery streams including the sampling and analysis of fugitive emissions. The program may be carried to Level II or III with an option for conducting split sample analyses.
Program B	Same as Program A, except that the fugitive sampling and analysis are not included.
Program A After First Time	Same as first time except that costs for repeated sampling and analyses of similar sources are reduced. Cost benefits are based on experience gained on previous sample, because reporting formats have been established, field equipment is available and operable, and because basic calibration data are available for compounds of interst.

Level I Program	For Level I only, the program has greatly simplified sampling, analysis, and reporting requirements. It will not be necessary to obtain completely representative samples. Separations will generally be incomplete and analyses will be less sensitive than those required at Level II. The primary objective of this program is to indicate the presence or absence of potentially hazardous classes of compounds in an uncharacterized stream.

Test Methods. Typical test methods available to the analyst and recommended for use in this problem are shown in Table 1.0-1. These methods are generally applicable to screening (Level I), qualitative (Level II), and quantitative (Level III) analyses for organic and inorganic materials. In practice these methods are matched with the fractions of the separated sample as needed.

Cost Analysis. Costs for operations are summarized on Table 1.0-2. Terms used to define the total costs for the various cases cited are described in Table 1.0-3.

Costs for Program A, in the first column are the highest, as would be expected. The most costly single element - that for direct sampling for fugitive emissions - is included. Also, this case includes all "first time" costs associated with equipment procurement, calibrations, analysis, and reporting. For analysis through Level II, including start-up, the cost is about $400,000. Cost through Level III on the same basis is about $450,000. Samples acquired for Level II are to be sufficient for Level III.

By omitting the fugitive emissions sample (Program B) Level II costs, including start up, drop to about $230,000. Level III costs on the same basis drop to about $270,000.

TABLE 1.0-1

RECOMMENDED ANALYTICAL TECHNIQUES

Screening Techniques

Inorganic Species	Organic Species
Microscopy	Gas Chromatography
Inorganic Spot Tests	High Resolution Mass Spectrometry
	Low Resolution Mass Spectrometry
	Infrared Spectrometry
	Organic Spot Tests

Qualitative Techniques

Inorganic Species	Organic Species
Spark Source Mass Spectrometry	Gas Chromatography-Mass Spectrometry
Optical Emission Spectrometry	High Resolution Mass Spectrometry
	High Pressure Liquid Chromatography
	Gas Chromatography

Quantitative Techniques

Inorganic Species	Organic Species
Atomic Absorption Spectrometry	Gas Chromatography
Ion Selective Electrodes	High Pressure Liquid Chromatography
	Gas Chromatography-Mass Spectrometry
	Mass Spectrometry
	Ultraviolet spectrometry

TABLE 1.0-2

SUMMARY OF COSTS

(in Thousands)

	Program A	Program B	Program A After First Time
Sampling	$50-60	$30-35	$50-60
Qualitative Analysis	70-85	45-55	55-60
Reporting	40-50	30-35	35-45
Replication	35	20	35
TOTAL LEVEL II	195-230	125-145	175-200
Quantitative Analysis	50	40	25
TOTAL LEVEL III	245-280	165-185	200-225
Additional Start-Up Expenses Associated with First Field Sampling	195	95	-

---

LEVEL I PROGRAM ONLY

Sampling	10-20
Analysis	10-30
Reporting	5
TOTAL LEVEL I	25-55
Additional Start-Up Costs	20-30

TABLE 1.0-3
DEFINITION OF TERMS USED IN TABLE 1.0-2

Cost Elements	Definition or Basis
Sampling Costs	Includes preparation, travel, on-site setup, actual sampling and on-site analysis, unpacking, repairs, and logging-in plus indirect cost of travel and subsistence. These costs are approximately 80 percent labor, 20 percent materials.
Analysis Costs	Includes all lab work on sample from extraction through separation to actual analysis as well as costs of chemicals, expendable laboratory items and instrument use charges. These costs are approximately 70 percent labor, 30 percent materials.
Reporting Costs	Includes all data reproduction, all correlations, all assessments and preparation of all reports. Costs are essentially 100 percent labor.
Replication Costs	For repeated analyses only. Does not include repeated sampling. They are lower than first-run costs because the time for qualitative analysis is reduced.
Start-Up Costs	Includes laboratory preparation and verification of techniques and preparation of a laboratory for on-site work as well as all hardware costs. This cost is approximately 25 percent labor.

The effects of duplicating the program with "first time" costs eliminated, are given in the third column. Costs through Level II are about $180,000, and through Level III about $210,000. Costs for this case, but with direct fugitive emission sampling eliminated, are not shown on the table; however, rough costs, by extrapolation, would be about $120,000 for Level II and for Level III, about $140,000.

Level I costs shown on the bottom are for a very limited program and are, as expected, much less costly than Level II and III analyses.

Appreciable reductions in Level III costs are noted in going from first to second time testing (from $450,000 to $210,000) and in going from first to second time testing with elimination of direct fugitive emission sampling (from $270,000 to $140,000).

Manpower. Table 1.0-4 lists the manpower requirements corresponding to the costs given in Table 1.0-2. This table indicates that of first time labor costs for Program A, 75 percent is spent on sampling, analysis, and reporting. In succeeding programs 90 percent of the labor cost is spent on these categories. The table also shows that the fugitive emission sample requires 35 percent of the total labor effort in sampling, analysis and reporting. The additional labor requirement is 330 mandays to obtain and analyze the direct fugitive emission sample.

Elapsed Time. The elapsed time to perform all activities for Program A would be 170 to 230 days. If fugitive emission sampling is omitted some 120 to 180 days would be required. Time periods required for various segments of activity, many conducted concurrently and some on a start/stop mode as required, are roughly as follows:

TABLE 1.0-4

SUMMARY OF MANPOWER REQUIREMENTS

(in man days)

	Program A	Program B	Program A After First Time
Sampling	190-225	110-125	190-225
Qualitative Analysis	200-260	115-165	130-160
Reporting	200-225	150-175	200-225
Replication	90	45	90
TOTAL LEVEL II	680-800	420-510	610-700
Quantitative Analysis	200	160	100
TOTAL LEVEL III	880-1000	580-670	710-800
Additional Start-Up Manpower Requirements	220	210	-

LEVEL I PROGRAM ONLY

Sampling	45-65
Analysis	30-65
Reporting	10-20
TOTAL LEVEL I	85-150
Additional Start-Up Requirement	100

Activity	Time Required, Total Days for Each Activity
Sampling	25 - 30
Analysis	50 - 65
Reporting	30 - 40
Replication	40 - 45
Start up	40 - 60

Conclusions

Sampling and analytical strategies for identifying potentially hazardous components in refinery streams are economically feasible. Cost analyses based on the use of proven analytical technology supports this conclusion.

The strategy is generally applicable to source sampling from liquid, solid, or gaseous streams. Sampling depends on the matrix, temperature, pressure and sampling location at the source, but options in the general procedures and in available equipment should enable the sampling teams to design their approach appropriately.

The methodologies used in this program should be applicable to the inspection of other refinery streams or to identification of compounds from other industrial sources such as coal conversion processes.

The sampling and analytical techniques and the equipment described in this report are readily available for implementation in refineries and other process plants.

1.0 INTRODUCTION

This report summarizes the development of a sampling and analytical strategy for the identification of potentially hazardous compounds in specific refinery effluents.

A wide range of expertise was required for collection, organization, and analysis of information for this program. The work included a detailed investigation into the nature and composition of refinery streams, the selection of sampling and analytical techniques, and estimates of analytical costs.

In order to benefit fully from the knowledge of specialists in these areas, EPA stipulated, in defining the scope of this program, that a number of contractors and consultants with known experience be retained to provide critical input during planning and review phases. To accomplish the program objectives with due emphasis on technical correctness, the following basic steps were followed.

- Radian Corporation, working with the EPA Task Officer, developed a work plan including: a) characterization of the five refinery streams, b) development of a sampling and analytical strategy suitable for the streams in question, c) estimates of the costs for testing based on use of the strategy, and d) critical review of the proposed strategies and costs by selected consultants.

- EPA Task Officer contracted with Battelle Columbus Laboratories, Arthur D. Little, Monsanto Research Corporation, Stanford Research Institute, and TRW, Inc., to work with EPA and Radian in the development of a sampling and analytical strategy. The intent was that each participant should contribute to the assembly of known technologies in such a manner as to produce a suitable and practical strategy.

- On the basis of stream compositions and sampling conditions specified by Radian, participating contractors provided input to the development of the strategy. Cost estimates based on the agreed-to strategy were then developed by the contractors.

- The results of these meetings were summarized by Radian in a preliminary report including a description of the strategy, estimates of testing costs, and a description of process analysis applied to each stream. These were sent to the EPA Task Officer for distribution within EPA offices. Copies of the draft were sent to consultants who had been retained to review the work.

- The final report, including comments from consultants, contractors, and EPA reviewers, was then prepared by Radian. Throughout the program, strong emphasis was placed on obtaining the best possible consensus of opinions from the experts retained for both technical and cost matters.

The information in this report was collected and analyzed for the sole purpose of demonstrating the feasibiity of a general sampling and analytical strategy. It is not intended to be used as a rigid formulation of protocol. It is intended as a guide to enable the researcher to consider the many aspects of the sampling and analysis problem. The methods shown on analytical flow sheets represent, in the opinion of the contributors of this report, reasonable and practical combinations of techniques for refinery stream analyses.

2.0 TECHNICAL APPROACH

This report consists of the following elements:

Volume I

Executive Summary	
Section 1.0	Introduction
Section 2.0	Technical Approach
Appendix A	Sampling and Analytical Techniques

Volume II

Appendix B	Process Analysis and Identification of Chemicals

The Executive Summary and Section 1.0 contain definitions of the program objectives and work plan and a summary of results and conclusions obtained from the work. This section, Technical Approach, contains a description of the methods used for developing the general sampling and analytical scheme, starting with a selection of available analytical techniques. Following this, the applicability of the general strategy to the five selected refinery streams is discussed. Finally, the costs for performing analysis of these streams are developed, based on best available estimates of equipment costs, procedure development costs, and manpower requirements.

Appendix A contains descriptions of the many sampling and analytical techniques considered in the general scheme. The details involved in sampling, separation, and analysis are discussed.

Appendix B contains a description of the steps by which the stream characterizations were derived. This includes the collection and classification of chemical data, a description of typical petroleum refinery operations, and a process analysis of operating units related to the five selected effluent streams.

Information on potentially hazardous chemicals in refinery streams obtained from the literature has been classified and listed in several tables in Appendix B. Table A is a classification of the toxicity of compounds found in refinery streams. Table B lists physical properties and concentrations of chemicals reported to be present in some twelve refinery streams. Tables C, D, and E are additional references to compounds cited for mutagenicity and toxicity.

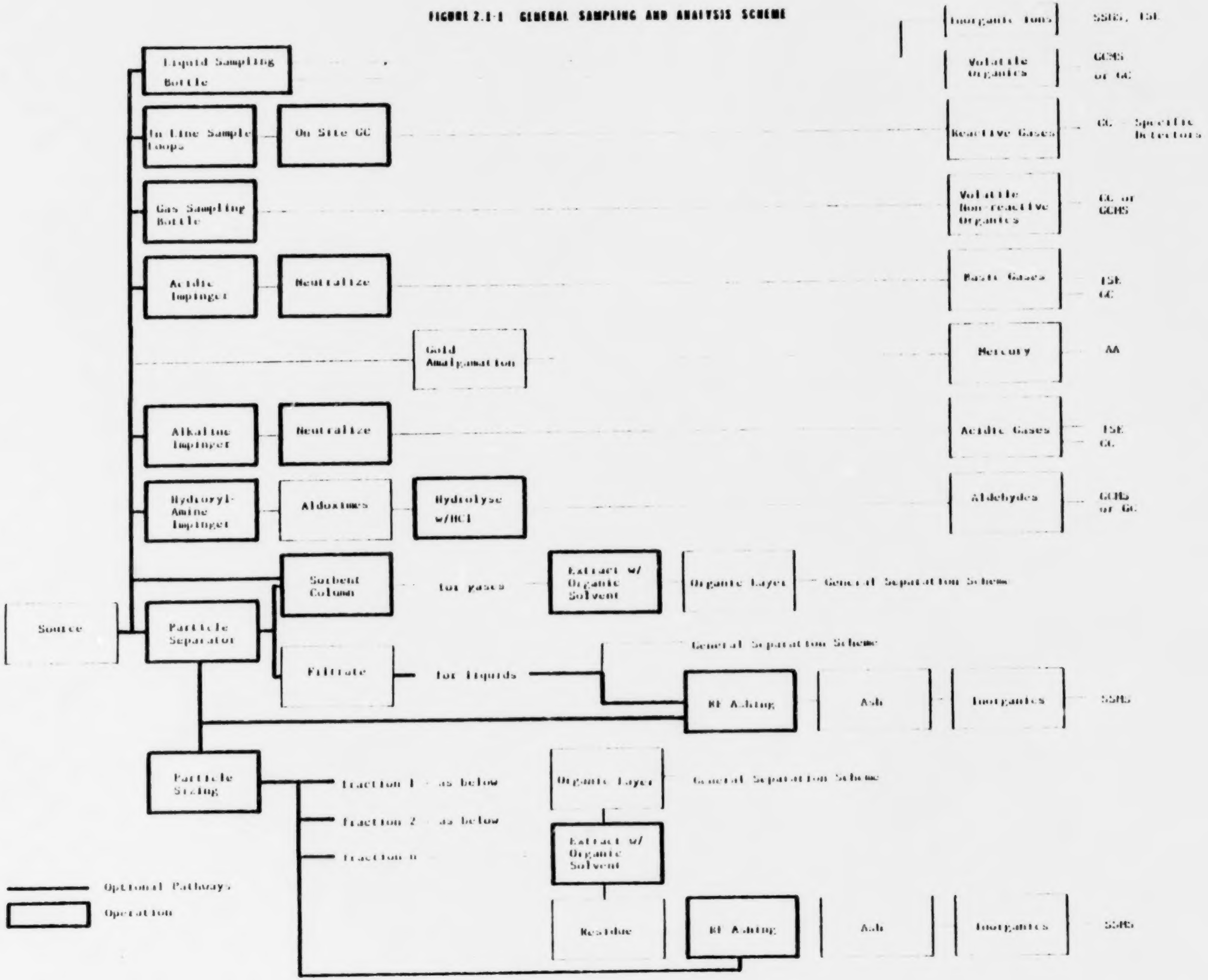
2.1 Sampling and Analytical Strategy

The sampling and analytical strategy developed during this program is presented in the following sections as a series of schemes; first a general scheme intended to be applicable to any source, followed by specific applications of that general scheme. The detail and verification for this section is presented in the Appendix.

2.1.1 General Scheme

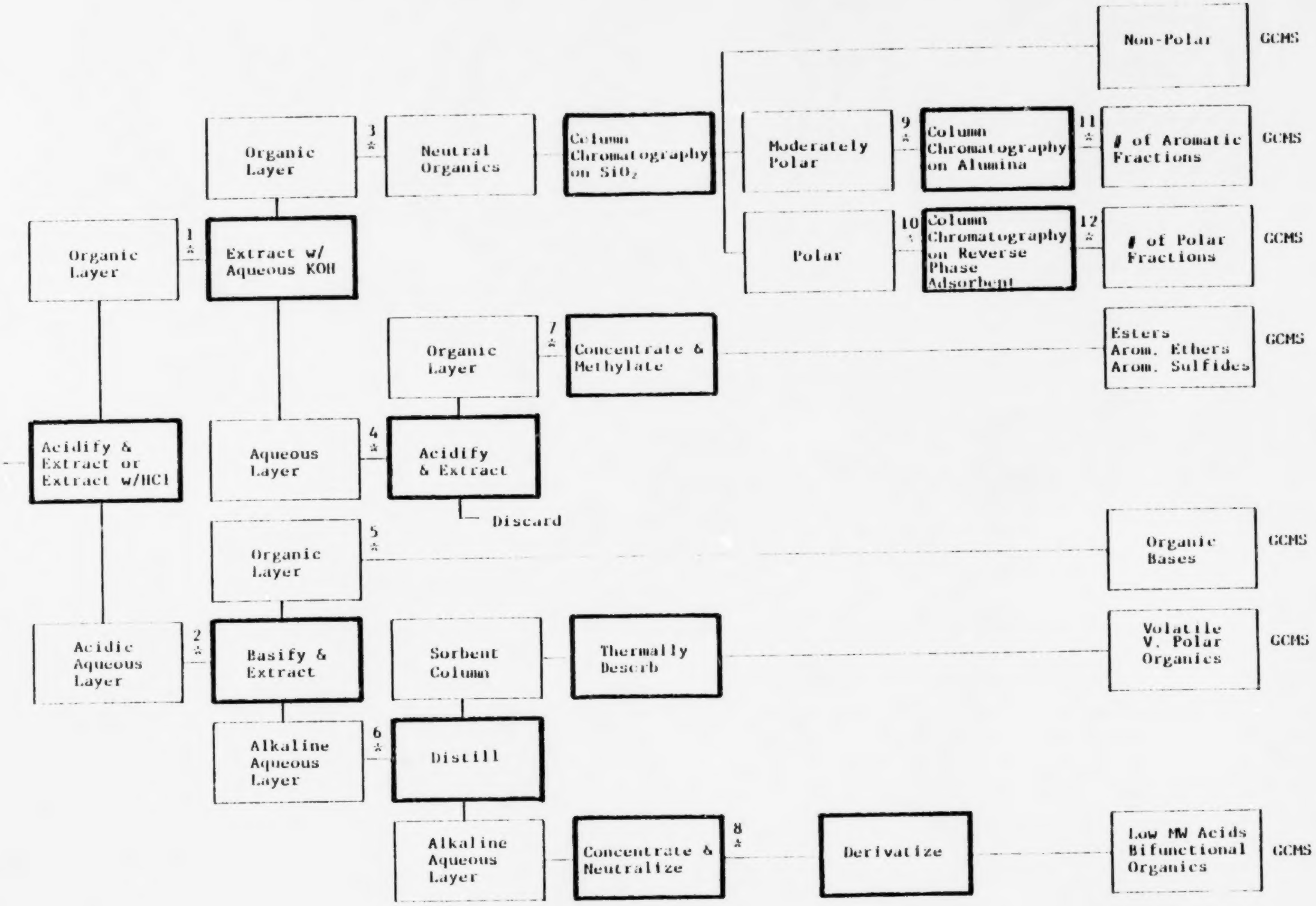
The general sampling and analytical scheme is given in Figures 2.1-1 and 2.1-2. The approach to sampling is intended to provide a number of optional pathways depending on the specific source to be sampled and the compounds of interest from that source. The heavy connecting lines in Figure 2.1-1 indicate the available options for sampling.

FIGURE 2.1-1 GENERAL SAMPLING AND ANALYSIS SCHEME



Source
Liquid Sampling Bottle
In Line Sample Loops
On Site GC
Gas Sampling Bottle
Acidic Impinger
Neutralize
Gold Amalgamation
Alkaline Impinger
Neutralize
Hydroxyl-Amine Impinger
Aldoximes
Hydrolyse w/HCl
Sorbent Column
for gases
Extract w/ Organic Solvent
Organic Layer
General Separation Scheme
Particle Separator
Filtrate
for liquids
General Separation Scheme
RF Ashing
Ash
Inorganics
SSMS
Particle Sizing
Fraction 1 - as below
Fraction 2 - as below
Fraction n
Organic Layer
General Separation Scheme
Extract w/ Organic Solvent
Residue
RF Ashing
Ash
Inorganics
SSMS
Inorganic Ions
SSMS, ISE
Volatile Organics
GCMS or GC
Reactive Gases
GC - Specific Detectors
Volatile Non-reactive Organics
GC or GCMS
Basic Gases
ISE GC
Mercury
AA
Acidic Gases
ISE GC
Aldehydes
GCMS or GC
Optional Pathways
Operation

FIGURE 2.1-2 GENERAL SEPARATION SCHEME


Organic Layer
Acidify & Extract or Extract w/HCl
Acidic Aqueous Layer
1 *
2 *
Organic Layer
Extract w/ Aqueous KOH
Aqueous Layer
Organic Layer
Basify & Extract
Alkaline Aqueous Layer
3 *
4 *
5 *
6 *
Neutral Organics
Organic Layer
Acidify & Extract
Discard
Sorbent Column
Distill
Alkaline Aqueous Layer
7 *
Column Chromatography on SiO2
Concentrate & Methylate
Thermally Desorb
Concentrate & Neutralize
8 *
Derivatize
Moderately Polar
Polar
9 *
10 *
Column Chromatography on Alumina
Column Chromatography on Reverse Phase Adsorbent
11 *
12 *
Non-Polar
# of Aromatic Fractions
# of Polar Fractions
Esters Arom. Ethers Arom. Sulfides
Organic Bases
Volatile V. Polar Organics
Low MW Acids Bifunctional Organics
GCMS
GCMS
GCMS
GCMS
GCMS
GCMS
GCMS

* Dec n p

The asterisks in Figure 2.1-2 indicate potential decision points encountered during the separation and analysis. These decisions are reached on the basis of (1) the desire to obtain knowledge about the components of a given fraction, and (2) the results of a screening test (Level I analysis). It should be noted that not all of the decision points would be used for any one sample.

Several levels of testing are available to the analyst. For the purposes of this report, the testing has been designated as: Level I - Tests for the presence or absence of classes, large groups of compounds or ions; Level II - Qualitative analysis for specific compounds plus qualitative and semiquantitative analysis for inorganic ions; and, Level III - Quantitative analysis of specific organic compounds or of groups of organic compounds, e.g., benzo [a] pyrene or total five-ring aromatics.

To apply the general scheme for sampling and analysis the sampling team and the analysis team must coordinate their efforts to insure that: proper sampling conditions are used; the correct amount of sample is acquired; the analyses for reactive materials are performed on site; and, samples for laboratory analysis are properly preserved.

Proper sampling conditions include: the use of inert materials for probes and collection devices (in-so-far as sampling conditions permit); proper temperature control of all parts of the collection system; the use of prewashed and pre-extracted materials in all possible situations; properly designed cyclones for particulate fractionation into the desired size ranges; appropriate intermittent or proportional samplers for liquid streams with potentially varying composition; and, the exclusion of air during the collection of liquid samples.

The proper amount of sample to collect will vary with the site; the concentration of the components of interest at the site; the level of interest[1] in a given component; and, the sensitivity of techniques available at the analysis facility. In general the sensitivity of measurement techniques is known, and the percent recoveries from the separation and concentration steps are known or can be approximated. Using the above information and defining a level of interest, one can calculate the degree of concentration necessary to obtain enough of the desired component for a complete analysis (assuming that the desired component is present at or above the level of interest). By applying the above technique to the component present at the lowest level, the sample mass or sampling time can be determined.

On-site analyses should be performed for all reactive materials. These analyses may include but are not limited to: gas chromatography for low molecular weight hydrocarbons, and sulfur and nitrogen containing species; ion specific electrodes for HCN, H_2S, NH_3 or HCl; and, special trapping and gas chromatographic or colorimetric analysis for aldehydes.

Sample preservation is one of the most important but least understood aspects of a generalized sampling scheme. Inability to preserve a sample often requires on-site or in-situ analyses. When this is impractical, the sample should be stored and shipped in the dark, at the lowest practical temperature and under vacuum or an inert gas.

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[1] The level of interest is the desired detection limit and may often vary from compound to compound. This factor profoundly influences cost.

The scheme for separation as presented in Figure 2.1-2 was chosen on the bases that: the distribution of compounds throughout the various fractions could be predicted with reasonable accuracy; it is feasible to conduct the early part of the separation under an inert atmosphere if that is necessary; the extractions do not involve elevated temperatures; the technology is well known; and, the number of fractions presented for analysis is minimal.

The purpose of the separation scheme is to effect a sufficient division of organic components so that those compounds of primary interest can be identified and quantitated by Level II and III analyses. This scheme does not intend to be the ultimate in separations and it is not intended that every compound collected in a sample will be isolated and identified. It is anticipated that the scheme shows a means of obtaining the maximum amount of correct information for a given money input.

The separation scheme (Figure 2.1-2) contains 12 decision points. By the examination of an infrared (IR) spectrum at point 1 the analyst can ascertain the presence or absence of major contributions from aliphatic, aromatic and acid species. At point 2 the analyst can apply functional group spot tests to determine the presence or absence of major contributions from basic organics and very polar water soluble compounds. At point 3 the analyst can use either or both of the above techniques to determine the presence or absence of aliphatic or aromatic components and, additionally, check the efficiency of the separation. In each case, the analyst may exercise an option of whether or not to proceed along the separation scheme or to attempt a quantitative analysis without further sample pretreatment. His decision will be based primarily on what he needs to learn about the sample. In many cases these may be the only decision points utilized.

Points 4, 5 and 6 indicate decisions similar to those at point 3 but involve different compound classes. In some cases it may not be necessary to perform further separations or to derivatize the compounds. At points 4 and 6 one of the available options is to use direct aqueous injection for GC-MS.

At point 7, the analyst should decide whether his mixture is sufficiently complex that further separation is required before GC-MS analysis or whether it is sufficient to methylate (and which reagent to use) and analyze the resulting derivatives simultaneously by GC-MS. The analyst would not use both points 4 and 7 in the same separation.

At point 8, the analyst should examine an IR spectrum to determine if derivatization is needed before GC-MS (low m.w. acids do not require derivatives, zwitterions do). If only acids are present, a GC analysis alone is sufficient. In some cases the bulk of the sample may be in this fraction and further separation or derivatization may be required. The separation would probably require column chromatography on ion exchange or standard adsorption supports.

At points 9 and 10 the analyst must decide whether to do a gas chromatography-mass spectrometry (GC-MS) analysis or to proceed through more column chromatography separations. The tests performed here would be IR or gas chromatography. At points 11 and 12 the analyst is being presented with a number of chromatographic fractions. At these points high-speed liquid chromatography, thin-layer chromatography, or gas chromatography may be used to select specific fractions for GC-MS.

Those techniques which are generally available to the analyst and which are recommended for this problem are shown in

Figure 2.1-3. The techniques are grouped according to the level of analysis required. In some cases the techniques appear on two levels but their application at the two levels would be different. For example, high-resolution mass spectrometry could be used at Level I to determine molecular weight ranges, types of compounds present and general complexity of the sample, while at Level II, when the sample is preseparated, high-resolution mass spectrometry might be used for qualitative analysis. The utility of this technique depends on the amount of discrimination used, the complexity of the sample and the amount and type of computer assistance available to the analyst. This technique is capable of generating too much data which in turn may make the analysis too confusing or too costly. Most of the Level I and II techniques are destructive and their use should be carefully considered if the available sample is at a minimum.

Throughout this scheme the approach has been developed to fit the components which would be found in petroleum refinery streams with the eventual intent of applying the scheme to coal conversion process streams (gasification or liquefaction). The types of streams available are expected to be similar at the two facilities. However, at this time, petroleum refinery streams are much better characterized and can provide an excellent testing ground for these schemes. Even in refinery streams, the analytical approach may be subject to change after the initial sampling and analysis because of experience gained during the first time. Thus, any scheme developed for repetitive sampling and analysis must leave provision for integrating previous experience. With this in mind, the above general sampling and analysis scheme has been theoretically tested on model refinery streams. The results of that testing are given in the following section.

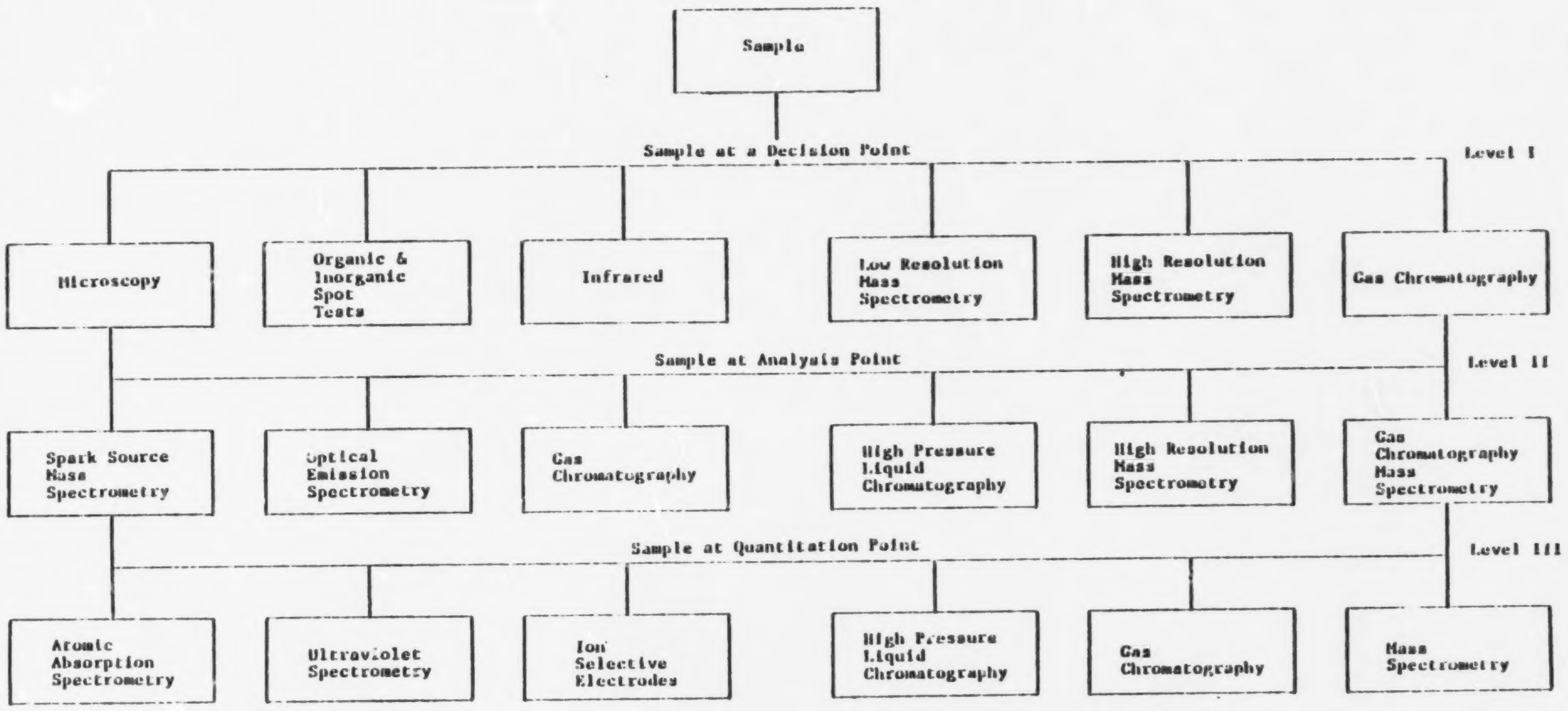

Sample
Sample at a Decision Point
Level I
Microscopy
Organic & Inorganic Spot Tests
Infrared
Low Resolution Mass Spectrometry
High Resolution Mass Spectrometry
Gas Chromatography
Sample at Analysis Point
Level II
Spark Source Mass Spectrometry
Optical Emission Spectrometry
Gas Chromatography
High Pressure Liquid Chromatography
High Resolution Mass Spectrometry
Gas Chromatography Mass Spectrometry
Sample at Quantitation Point
Level III
Atomic Absorption Spectrometry
Ultraviolet Spectrometry
Ion Selective Electrodes
High Pressure Liquid Chromatography
Gas Chromatography
Mass Spectrometry

FIGURE 2.1-3 **RECOMMENDED ANALYTICAL TECHNIQUES**

2.1.2 Specific Applications of the General Scheme

For purposes of discussion the refinery streams have been categorized as process streams (organic liquid matrix), water matrix streams, and as streams containing vapor and particulate. The following discussion will show the range of applicability of the general scheme.

2.1.2.1 Process Streams From the Atmospheric Still

Streams from the atmospheric still have been chosen as a model because they: (1) represent the range of volatilities to be encountered in a refinery; (2) represent the range of complexities of component mixtures available in process streams; and (3) represent a typical source of fugitive emissions.

Light Ends. The sample matrix is light hydrocarbon gases from methane through n-butane. A summary of potential emissions is given in Table 2.1-1. The gaseous sample can be taken from a tap in the discharge line from the light ends compressor. With the possible exception of small amounts of condensate which may be found on the walls of a sample bottle, the sample is expected to be entirely gaseous. The sampling and analysis scheme for the hazardous components of this stream is presented in Figure 2.1-4.

The in-line loops should be constructed of a fluorocarbon polymer as should the components of the on-site gas chromatograph. The expected reactive gases would be either nitrogen or sulfur containing and would require selective detectors - either Hall conductivity for nitrogen or flame photometric for sulfur.

TABLE 2.1-1

FUGITIVE LIGHT ENDS EMISSIONS FROM ATMOSPHERIC DISTILLATION COLUMN

A. Major Components (Non-Pollutants)

Component	Vol. %	TLV (ppm)	Reference
Methane	C.2	10,000	RO-188
Isobutane	31.0	-	WA-074

B. Known to be hazardous and known to be present.

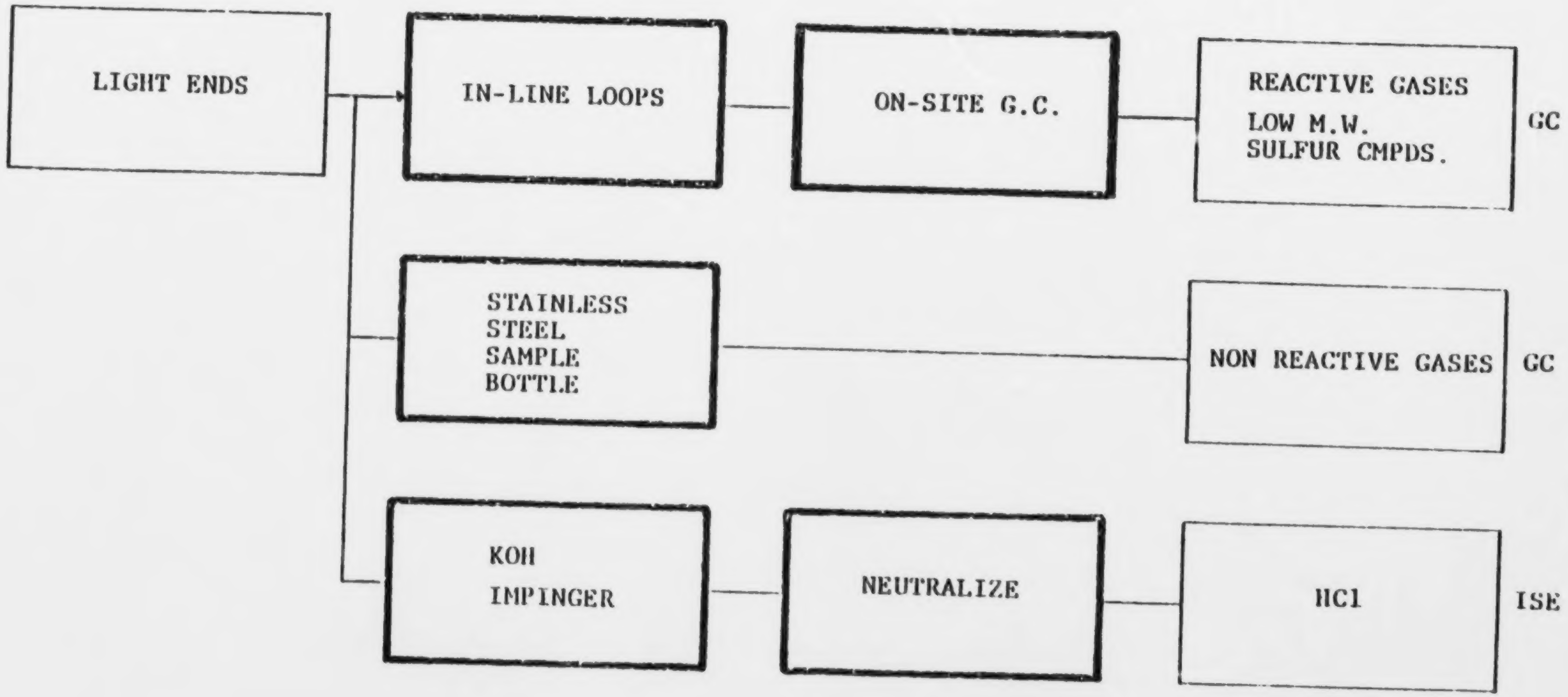
Pollutant	Vol. %	TLV (ppm)	Reference
n-Butane	48.6	500	WA-074
Propane	19.6	500	WA-074
Ethane	1.5	500	WA-074
H_2S	1.0	10	PE-140, HA-316
HCl	0.7	5	PE-140
Methanethiol	0.2	0.5	BE-147, GR-123

C. Potentially hazardous if present.

Pollutant	Vol. %	TLV (ppm)	Reference
Ammonia		25	ME-107, KL-032

FIGURE 2.1-4

STREAM 1A - LIGHT ENDS FROM ATMOSPHERIC STILL


LIGHT ENDS
IN-LINE LOOPS
ON-SITE G.C.
REACTIVE GASES
LOW M.W.
SULFUR CMPDS.
GC
STAINLESS
STEEL
SAMPLE
BOTTLE
NON REACTIVE GASES
GC
KOH
IMPINGER
NEUTRALIZE
HCl
ISE

The stainless steel bottle can, in this case (because temperatures are low), be coated with a fluorocarbon polymer to reduce surface interaction with the sample. The bottle is preferred over an inert sampling bag because of the pressurized sample line and because a bottle may be heated to revaporize any condensed material. If possible, this sample should be analyzed on site using a gas chromatograph with a flame ionization detector. Hydrocarbon components not detected by the in-line gas chromatographs would be detected here.

The KOH impinger will trap the two suspected acid gases, HCl and H_2S, along with mercaptans. The impinger contents can be neutralized and the Cl^- concentration can be measured with an ion selective electrode.

Naphtha Cut. The sample matrix is C_5 to C_{10} aliphatic, cycloaliphatic and aromatic hydrocarbons. A summary of potential emissions is given in Table 2.1-2. The liquid sample can be taken from the discharge of the naphtha stream pump. The sample will be liquid but may contain dissolved low-boiling components. The sampling and analysis scheme for the hazardous components of this stream is presented in Figure 2.1-5.

The sample should be taken in a fluorocarbon polymer-lined, stainless steel bottle.

A portion of the sample should be analyzed on site for reactive sulfur species by gas chromatography with a sulfur selective detector. The remainder of the sample should be preserved for laboratory analysis.

TABLE 2.1-2

FUGITIVE NAPHTHA EMISSIONS FROM ATMOSPHERIC DISTILLATION COLUMN

A. Major Components

Components	Vol. %	TLV (ppm)	Reference
C_5 to C_{10} Paraffins	40.0		GR-123
C_5 to C_{10} Cycloparaffins	40.0		GR-123
Aromatics	20.0		GR-123

B. Known to be hazardous and known to be present.

Pollutant	Vol. %	TLV (ppm)	Reference
C_5 to C_8 n-Alkanes	16.9-25.7	100-600	RO-189, CA-227
Cyclopentane	0.14-1.3	-[a]	RO-189
Cyclohexane	1.83-10.7	300	RO-189
Methylcyclohexane	0.35-17.5	400	RO-188, RO-189
Benzene	0.2 -1.23	10	CA-227, RO-189
Toluene	1.0 -7.4	100	CA-227, RO-189
Xylenes	3.51-9.92	100	RO-189
Ethylbenzene	0.19-0.93	100	RO-188. RO-189
Isopropylbenzene	0.12-0.33	50	RO-189
1,2,3-Trimethylbenzene	0.56	25	RO-188
1,3,5-Trimethylbenzene	0.32-1.34	35	RO-189
Ethanethiol	0.03	0.5	GR-123
2-Butanethiol	0.02	0.5	GR-123
Mercaptans	∿0.10	-[b]	GR-123

C. Potentially hazardous if present.

Pollutant	Vol. %	TLV (ppm)	Reference
C_1 to C_4 Alkanoic Acids		5-10	LO-112
Cyclohexane		300	RO-189
2,2,4-Trimethylpentane		-[a]	RO-189
Pyridine		5	PE-140
Alkyl Pyridines[c]		-[a]	BR-325
Pyrrole		-[a]	PE-140
Trace Metals		-[d]	VO-027

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[a] Rated as moderately toxic (SA-175).

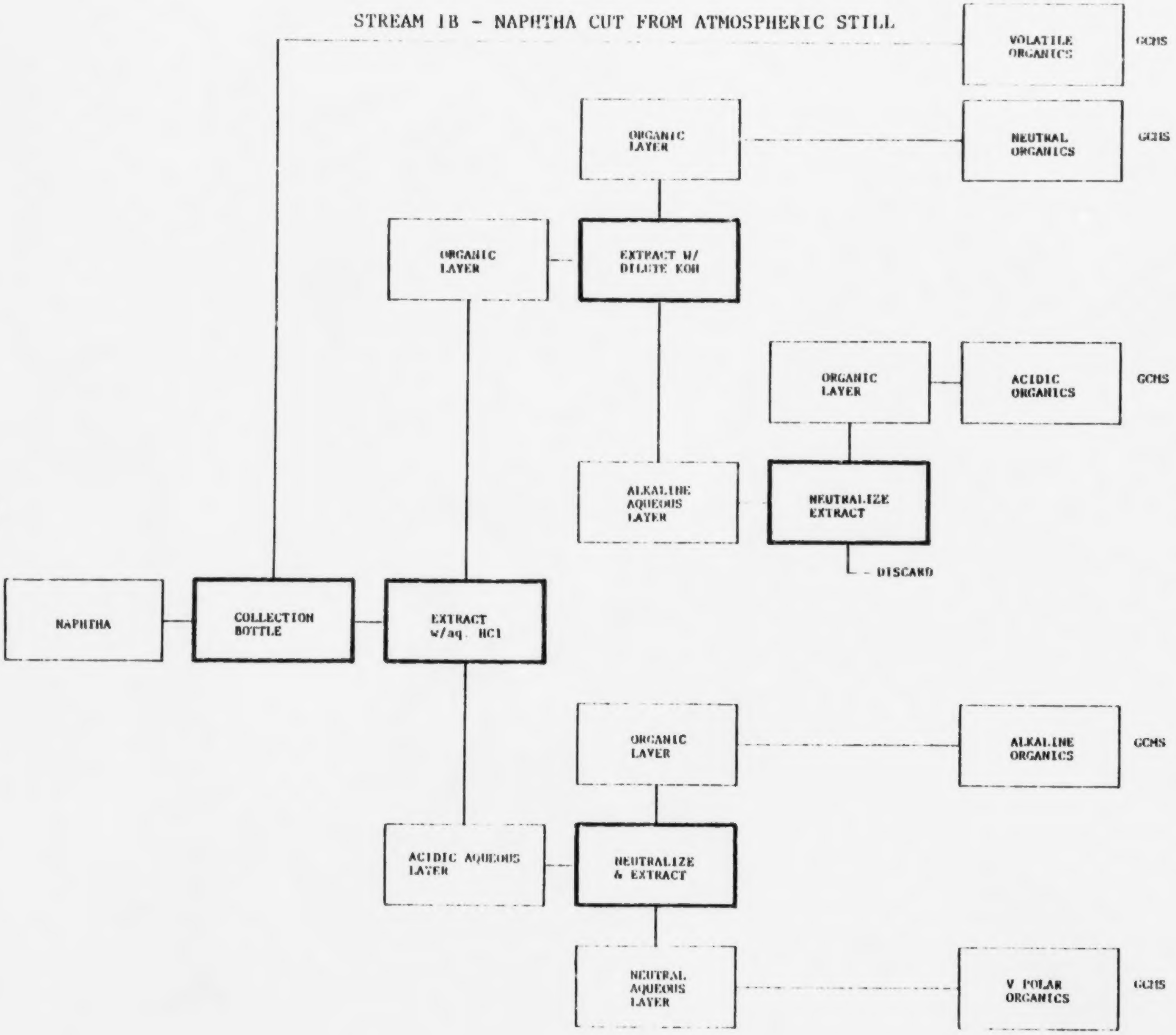
[b] All mercaptans are considered toxic.

[c] No TLV data, but assumed as hazardous as pyridine.

[d] Refer to Volume II, Appendix B, Section 2.2.1 for the complete trace metals listing.

FIGURE 2.1-5

STREAM IB - NAPHTHA CUT FROM ATMOSPHERIC STILL


VOLATILE ORGANICS
GCMS
ORGANIC LAYER
NEUTRAL ORGANICS
GCMS
ORGANIC LAYER
EXTRACT W/ DILUTE KOH
ORGANIC LAYER
ACIDIC ORGANICS
GCMS
ALKALINE AQUEOUS LAYER
NEUTRALIZE EXTRACT
DISCARD
NAPHTHA
COLLECTION BOTTLE
EXTRACT w/aq. HCl
ORGANIC LAYER
ALKALINE ORGANICS
GCMS
ACIDIC AQUEOUS LAYER
NEUTRALIZE & EXTRACT
NEUTRAL AQUEOUS LAYER
V POLAR ORGANICS
GCMS

In the laboratory, the column chromatographic portion of the separation scheme is not required because the neutral organics in this hydrocarbon cut have all previously been separated with a single capillary column for gas chromatography. The bulk of the sample will remain in the neutral fraction.

The acidic aqueous layer will contain the pyridines and any other basic organic compounds in the sample, because these compounds should form hydrochloride salts. Basifying and extraction of this aqueous layer with an appropriate organic solvent will remove the nitrogen-containing compounds which can be determined by gas chromatography. The very polar organics such as formic and acetic acid will remain in the aqueous layer. Subsequent neutralization will allow the acids to be chromatographed from the aqueous solution.

The alkaline aqueous layer resulting from the second extraction of the matrix will contain higher molecular weight thiols and organic acids (C_1-C_5 and C_3- C_5 respectively). These can be chromatographed without further treatment.

Distillate Cut. The sample matrix is composed of C_{11}-C_{15} hydrocarbons, primarily paraffins and cycloparaffins. A summary of the potential emissions is given in Table 2.1-3. The sample would be taken as for the naphtha cut. The sampling and analysis scheme is presented in Figure 2.1-6.

All separation and analyses should be performed in the laboratory.

The separation scheme here differs from the previous scheme by the addition of a column chromatographic separation of

TABLE 2.1-3

FUGITIVE DISTILLATE EMISSIONS FROM ATMOSPHERIC DISTILLATION COLUMN

A. Major Components

Components	Vol. %	TLV (ppm)	Reference
C_{11} to C_{15} Paraffins	40.0		GR-123
C_{11} to C_{15} Cycloparaffins	45.0		GR-123
C_{11} to C_{15} Aromatics	15.0		GR-123

B. Known to be hazardous and known to be present.

Pollutant	Vol. %	TLV (ppm)	Reference
1,2,3-Trimethylbenzene	.44	25	RO-188
1,2,3,4-Tetrahydronaphthalene	.11	25	RO-189
Naphthalene	.06	10	RO-188

C. Potentially hazardous if present.

Pollutant	Vol. %	TLV (ppm)	Reference
1-Methyl-4-isopropylbenzene		50	NA-231
2-Methylnaphthalene		-[a]	RO-188
Indoles		carcinogens	PE-140
Phenol		5	BE-147
Cresols		5	FI-083
Naphthol		-[b]	LO-112
Biphenyl		0.2	RO-188
Quinoline		-[c]	BA-325
Alkyl Quinolines		-[d]	BA-325
Alkyl Pyridines		-[e]	BA-325
Octanethiol		-[c]	GR-123
Trace Metals		-[f]	AN-104, VO-027

---

a. Limited experiments suggest high toxicity.

b. Rated as moderately toxic (SA-175).

c. Rated as severely toxic (SA-175).

d. Assumed similar in toxicity to quinoline.

e. Some alkyl pyridines have been described as highly toxic.

f. Refer to Volume II, Appendix B, Section 2.2.1, for the complete trace metals listing.

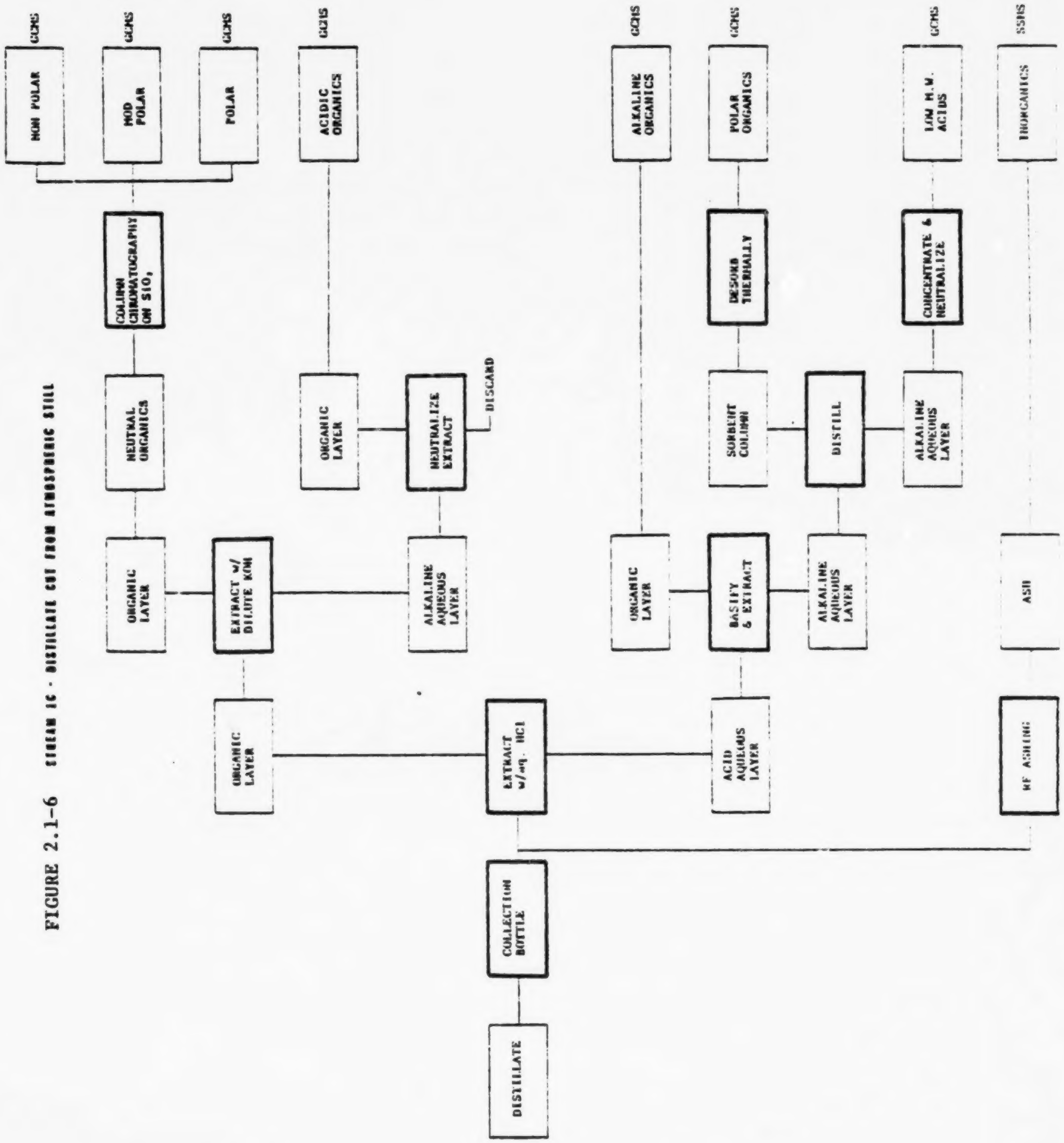

DISTILLATE
COLLECTION BOTTLE
EXTRACT w/aq. HCl
ORGANIC LAYER
ACID AQUEOUS LAYER
EXTRACT w/ DILUTE KOH
ORGANIC LAYER
ALKALINE AQUEOUS LAYER
NEUTRAL ORGANICS
COLUMN CHROMATOCRAPHY ON SIO,
NON POLAR
MOD POLAR
POLAR
GCMS
GCMS
GCMS
NEUTRALIZE EXTRACT
DISCARD
ORGANIC LAYER
ACIDIC ORGANICS
GCMS
BASIFY & EXTRACT
ORGANIC LAYER
ALKALINE ORGANICS
GCMS
ALKALINE AQUEOUS LAYER
DISTILL
SORBENT COLUMN
DESORB THERMALLY
POLAR ORGANICS
GCMS
ALKALINE AQUEOUS LAYER
CONCENTRATE & NEUTRALIZE
LOW M.W. ACIDS
GCMS
RF ASHING
ASH
INORGANICS
SSMS

FIGURE 2.1-6 STREAM 1C - DISTILLATE CUT FROM ATMOSPHERIC STILL

the neutral fraction; and, a further separation of the very polar water-soluble organics which remain in the aqueous layer from the first HCl extraction.

The column chromatographic separation of the neutral fraction utilizes silica gel to obtain three subfractions which contain alkanes + alkenes, alkenes + alkyl sulfides + aromatics + aromatic sulfides, and nitrogen and oxygen heterocyclics respectively. The separation of the fractions is relatively clean. These fractions should be amenable to immediate analysis by gas chromatography.

Further separation of the water-soluble fraction becomes necessary as the number of possible types of water soluble compounds increases, e.g., zwitterionic species. Esterification of the very polar fraction may be required in order for chromatography to be effective.

The acidic organic fraction acquired from the second aqueous extract of the distillate cut will contain organic acids, phenols and thiols. It may be necessary to methylate this group of compounds in order to achieve good chromatographic separation.

A portion of the original sample should be set aside. Inorganic analysis should be performed on this portion because the organo metallic compounds should still be intact. Since nothing has been added to the sample, the risk of contamination is minimal. Low-temperature radio frequency (RF) ashing of the sample should minimize sample loss due to volatilization.

Gas Oil Cut. The sample matrix is hydrocarbon - ranging from C_{15}-C_{25}, as shown in Table 2.1-4. Other potential emissions are also shown in this table. The sample will be collected as described for the naphtha cut. The sampling and analysis scheme is presented in Figure 2.1-7.

Although the listed hazardous organic chemicals should all be found in the moderately polar, column chromatographic cut of the neutral fraction, this sample should also have several sulfur, oxygen and nitrogen-containing components. The suggested separation scheme allows the analyst to do a crude fractionation of these latter components.

This scheme differs from previous schemes in that: (1) it requires the complete separation of the neutral fraction; (2) it requires dilution of the original sample with a volatile non-hydrocarbon solvent; and (3) no significant water soluble components are anticipated.

Complete separation of the neutral fraction will be required because of the large amount of aromatics in the sample. A linear elution, liquid chromatographic fraction of the moderately polar fraction will be required. The number of fractions collected for analysis is left to the discretion of the analyst.

Further separation of the polar fraction from column chromatography on silica gel will also be required. This can be done by reversed-phase chromatography on an ODS treated support such as Porasil C-18. Again, the number of cuts of the nitrogen- and oxygen-containing compounds is left to the discretion of the analyst.

TABLE 2.1-4

FUGITIVE GAS OIL EMISSIONS FROM ATMOSPHERIC DISTILLATION COLUMN

A. Major Components

Components	Vol. %	TLV (ppm)	Reference
C_{15} to C_{25} Paraffins	30.0		GR-123
C_{15} to C_{25} Cycloparaffins	50.0		GR-123
C_{15} to C_{25} Aromatics	20.0		GR-123

B. Known to be hazardous and known to be present.

Pollutant	Vol. %	TLV (ppm)	Reference
Phenanthrenes	-[a]	carcinogens	CA-228
Perylenes	-[a]	carcinogens	CA-228
Benzanthracenes	-[a]	carcinogens	TY-008
Chrysenes	-[a]	carcinogens	TH-086
Pyrenes	-[a]	carcinogens	DO-074

C. Potentially hazardous if present.

Pollutant	Vol. %	TLV (ppm)	Reference
Anthracene		0.01 mg/m^3	DO-074
Trace Metals[b]		-	AN-104

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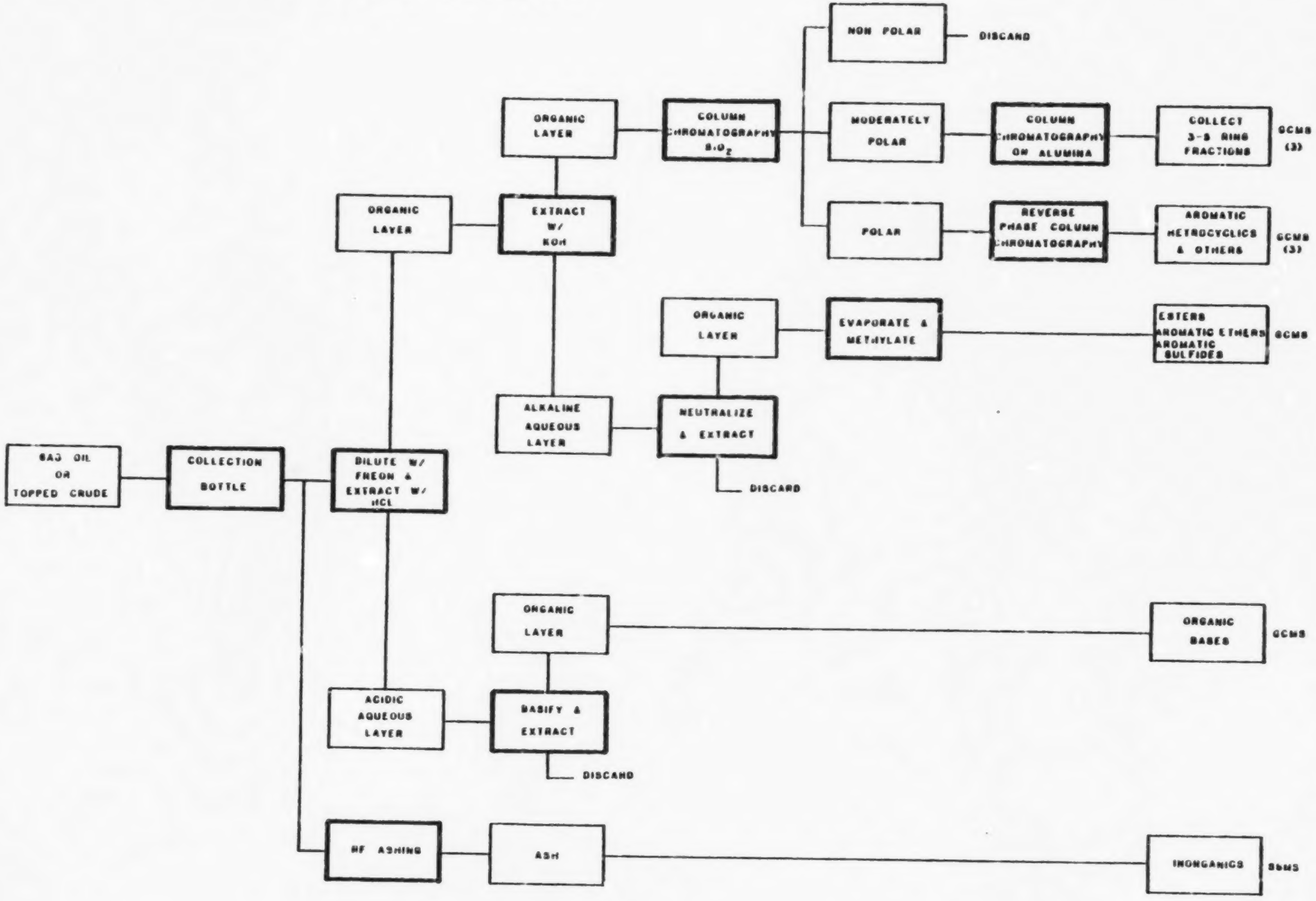
a. Cited in literature as being present, and therefore it is deemed a hazard.

b. Refer to Volume II, Appendix B, Section 2.2.1, for the complete trace metals listing.

FIGURE 2.1-7

STREAMS 1D & 1E

GAS OIL CUT AND TOPPED CRUDE FROM ATMOSPHERIC STILL


GAS OIL OR TOPPED CRUDE
COLLECTION BOTTLE
DILUTE W/ FREON & EXTRACT W/ HCL
ORGANIC LAYER
EXTRACT W/ KOH
ORGANIC LAYER
COLUMN CHROMATOGRAPHY SiO_2
NON POLAR
DISCAND
MODERATELY POLAR
COLUMN CHROMATOGRAPHY ON ALUMINA
COLLECT 3-5 RING FRACTIONS
GCMS (3)
POLAR
REVERSE PHASE COLUMN CHROMATOGRAPHY
AROMATIC HETROCYCLICS & OTHERS
GCMS (3)
ALKALINE AQUEOUS LAYER
NEUTRALIZE & EXTRACT
DISCARD
ORGANIC LAYER
EVAPORATE & METHYLATE
ESTERS AROMATIC ETHERS AROMATIC SULFIDES
GCMS
ACIDIC AQUEOUS LAYER
BASIFY & EXTRACT
DISCAND
ORGANIC LAYER
ORGANIC BASES
GCMS
HF ASHING
ASH
INORGANICS
SSMS

The viscosity of the gas oil cut will probably necessitate that the sample be diluted with freon before attempting liquid partitioning steps. Freon is preferred because of its properties as a solvent, its volatility and because it will generally be free of hydrocarbon impurities.

In a cut of the molecular weight range expected in this sample, no water soluble components are expected - zwitterionic or otherwise.

The organic layer containing the acidic compounds should be methylated to form methyl esters from carboxylic acids, methyl aromatic ethers from phenolic hydroxyl groups and methyl aromatic sulfides from thiophenols. The primary reason for this is to facilitate the chromatography.

Topped Crude. The matrix for this sample is C_{25} and heavier hydrocarbons. The matrix will be 30 percent aromatic and the polynuclear compounds will probably have 5 or more rings. The potential emissions are shown in Table 2.1-5. The sampling and analyses are essentially identical with those described for the gas oil. The separations will be more difficult because of the asphaltic components of the sample and more dilute solutions in freon may be necessary. All of the sample must be in solution in freon in order to accomplish the liquid-liquid partitioning.

2.1.2.2 Streams With a Predominantly Water Matrix

Streams which are aqueous or predominantly aqueous are sampled in a fashion similar to organic liquid streams. If the stream is homogeneous and substantially invariant it can be grab sampled. If the stream is heterogeneous or of varying composition,

TABLE 2.1-5

FUGITIVE TOPPED CRUDE EMISSIONS FROM ATMOSPHERIC DISTILLATION COLUMN

A. Major Components

Components	Vol. %	TLV (ppm)	Reference
$>C_{25}$ Paraffins	20.0		GR-123
$>C_{25}$ Cycloparaffins	45.0		GR-123
$>C_{25}$ Aromatics	30.0		GR-123
Residue	5.0		GR-123

B. Known to be present and known to be hazardous.

Pollutant	Vol. %	TLV (ppm)	Reference
Benzopyrenes	-[a]	carcinogens	TH-086
Benzfluorenes	-[a]	carcinogens	TY-008
Benzanthracenes	-[a]	carcinogens	TY-008
Fluoranthenes	-[a]	carcinogens	TY-008
Alkyl Pyrenes	-[a]	carcinogens	DO-074

C. Potentially hazardous if present.

Pollutant	Vol. %	TLV (ppm)	Reference

None, only the carcinogens mentioned above are believed to be hazardous mainly due to the very low vapor pressure of the topped crude components.

---

[a] Cited in literature as being present, and therefore, it is deemed a hazard.

it should be sampled with an intermittent or proportional sampler. For the analyst, the primary difference between an aqueous and a non-aqueous stream is that the components of interest in an aqueous stream are usually easier to separate from the sample matrix.

Condensate from Atmospheric Still. The condensate from the atmospheric still is primarily water and is sampled at the discharge point from the pump to the sewer lines leading to the API separator. The stream is described in Table 2.1-6 The sampling and analysis scheme for this stream is given in Figure 2.1-8.

The scheme calls for on-site measure of ammonia as free ammonia by a selective electrode technique. There are no potential interferences for this measurement. It is highly unlikely that free HCl would be found in this stream, however, if the stream is acidic the pH can be recorded, the chloride concentration can be measured as previously described, and assuming all acidity is due to HCl, its concentration can be calculated.

A filtration step has been included in the event the stream contains solid organic matter. If sufficient solid material has been collected on the filter it should be extracted with an organic solvent. The solvent should then be used to extract the acidified filtrate. The extracted solids should be examined by infrared for insoluble organics (polymers) and ashed in preparation for inorganic analysis by spark source mass spectrometry. If no solids are found in the sample, a portion of the original sample should be evaporated and analyzed by spark source mass spectrometry. In the event that solids were filtered out of the sample, a portion of the filtrate should be presented for inorganic analysis.

TABLE 2.1-6

ATMOSPHERIC STILL CONDENSATE

A. Major Components (Non-Pollutants)

Component	Vol. %	TLV (ppm)	Reference
Water	98-99+		BE-147

B. Known to be present and known to be hazardous.

Pollutant	Concentration (ppm)	TLV[a] (ppm)	Reference
Phenol	0-20	5	BE-147
Sulfides	100-5,000	10[b]	BE-147
Ammonia	300-2,000	25	BE-147
Oil	100-200	-	BE-147

C. Potentially hazardous if present.

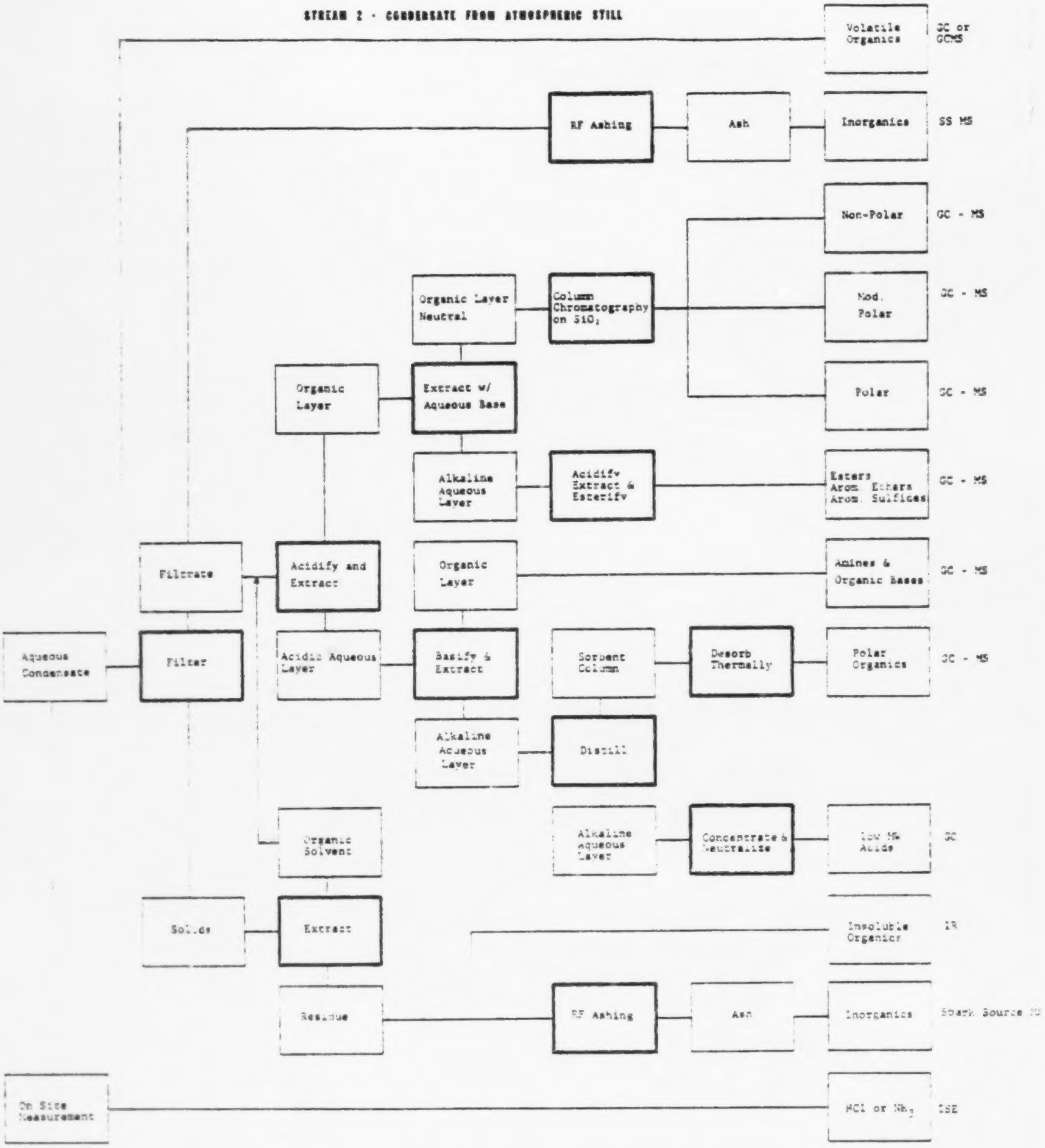
Pollutant	Concentration (ppm)	TLV[a] (ppm)	Reference
C_4 to C_8 n-Alkanes		100-600	CA-227, RO-189, SM-094
Cyclohexane		300	SM-094
Methylcyclohexane		400	SM-094
Benzene		10	SM-094
Toluene		100	SM-094
Xylenes		100	SM-094
Ethylbenzene		100	SM-094
Isopropylbenzene		50	SM-094
Trimethylbenzenes[f]		25-35	RO-189
Acetic Acid		10	LO-112
Formic Acid		5	LO-112
Phenol		5	BE-147
Cresols		5	BE-147
Pyridine		5[c,d]	LO-112
Alkyl Pyridines		-[d]	LO-112
Pyrrole		-	PE-140
C_1 to C_3 thiols		0.5	GR-123
Chlorides		5[e]	PE-140
Salts[f]		-	PE-140
Trace Metals[f]		-	PE-140

---

a. To be used as a guideline for determining relative toxicity.
b. This is the TLV for H_2S gas.
c. Some alkyl pyridines have been described as highly toxic.
d. Rated as moderately toxic (SA-175).
e. This is the TLV for HCl gas.
f. Refer to Volume II, Appendix B, Section 2.2.2, for the complete listing.

FIGURE 2.1-8

STREAM 2 - CONDENSATE FROM ATMOSPHERIC STILL


Volatile Organics
GC or GCMS
RF Ashing
Ash
Inorganics
SS MS
Non-Polar
GC - MS
Organic Layer Neutral
Column Chromatography on SiO_2
Mod. Polar
GC - MS
Organic Layer
Extract w/ Aqueous Base
Polar
GC - MS
Alkaline Aqueous Layer
Acidify Extract & Esterify
Esters Arom. Ethers Arom. Sulfides
GC - MS
Filtrate
Acidify and Extract
Organic Layer
Amines & Organic Bases
GC - MS
Aqueous Condensate
Filter
Acidic Aqueous Layer
Basify & Extract
Sorbent Column
Desorb Thermally
Polar Organics
GC - MS
Alkaline Aqueous Layer
Distill
Organic Solvent
Alkaline Aqueous Layer
Concentrate & Neutralize
Low MW Acids
GC
Solids
Extract
Insoluble Organics
IR
Residue
RF Ashing
Ash
Inorganics
Spark Source MS
On Site Measurement
HCl or NH_3
ISE

A portion of the original sample should be analyzed by GC-MS for volatile materials. This analysis should be completed before filtration or any other separation step is attempted. Not only will the measurement detect volatile components which could be lost in succeeding steps, but often it will provide information on the degree of separation required thus relieving the analyst of further testing at decision points.

The filtrate (or the original sample if no solids were present) should be acidified and extracted with fresh organic solvent (or the solvent used to extract the solids, when available). The liquid-liquid partitioning scheme is then the same as discussed in earlier sections.

The primary decision point with this sample involves whether or not to use a column chromatographic separation of the neutrals fraction. It is quite likely that this fraction can go directly to a GC-MS analysis. A simple GC run should be sufficient as a Level I analysis.

A second pertinent decision point involves the methylation of the acid organics. This may not be required if the fraction does not appear complex.

Effluent From the API Separator. Again, the sample matrix is water. As shown in Table 2.1-7, the sample differs from the previous one in its increased complexity and in the higher probability that the sample may be heterogeneous. For the latter reason, the recommended method of sampling is by use of an automated intermittent liquid sampler. The sampling and analysis scheme is shown in Figure 2.1-9.

TABLE 2.1-7

API SEPARATOR EFFLUENT

A. Major Components

Component	Vol. %	TLV (ppm)	Reference
Water	98-99+		AM-062

B. Known to be hazardous and known to be present.

Pollutant	Concentration (ppm)	TLV (ppm)[a]	Reference
Phenol	11.4	5	AM-041
Sulfides	11.3	10 (as H_2S)	AM-041
Phosphorous	0.5	0.1	AM-041
Ammonia	60.0	25	AM-041

C. Potentially hazardous if present.

Pollutant	Concentration (ppm)	TLV (ppm)[a]	Reference[b]
Formic Acid		5	-
Acetic Acid		5	-
HCl		10	BE-147
Naphthanoic Acid		-[c]	BU-159
Pyridine		5	-
Ammonia		25	BE-147
C_1 to C_3 thiols		0.5	-
Cresols		5	KE-151
Formaldehyde		2	-
Benzene		10	-
Toluene		100	-
Xylene		100	-
Alkyl Benzenes[d]		25 - 100	-
Naphthalene		10	-
Tetrahydro-naphthalene		25	-
Decahydro-naphthalene		50	-
Biphenyl		0.2	-
Anthracene		0.1 mg/m^3	-
Cyclohexane		300	BU-159
C_2 to C_8 n-Alkanes		100 - 600	-
Methylbutenes		-	-
1-Hexene		-	-
Polynuclear aromatics[d]		carcinogens	-
Trace Metals[d]		-	-

---

a. The TLV given is for concentrations in air.

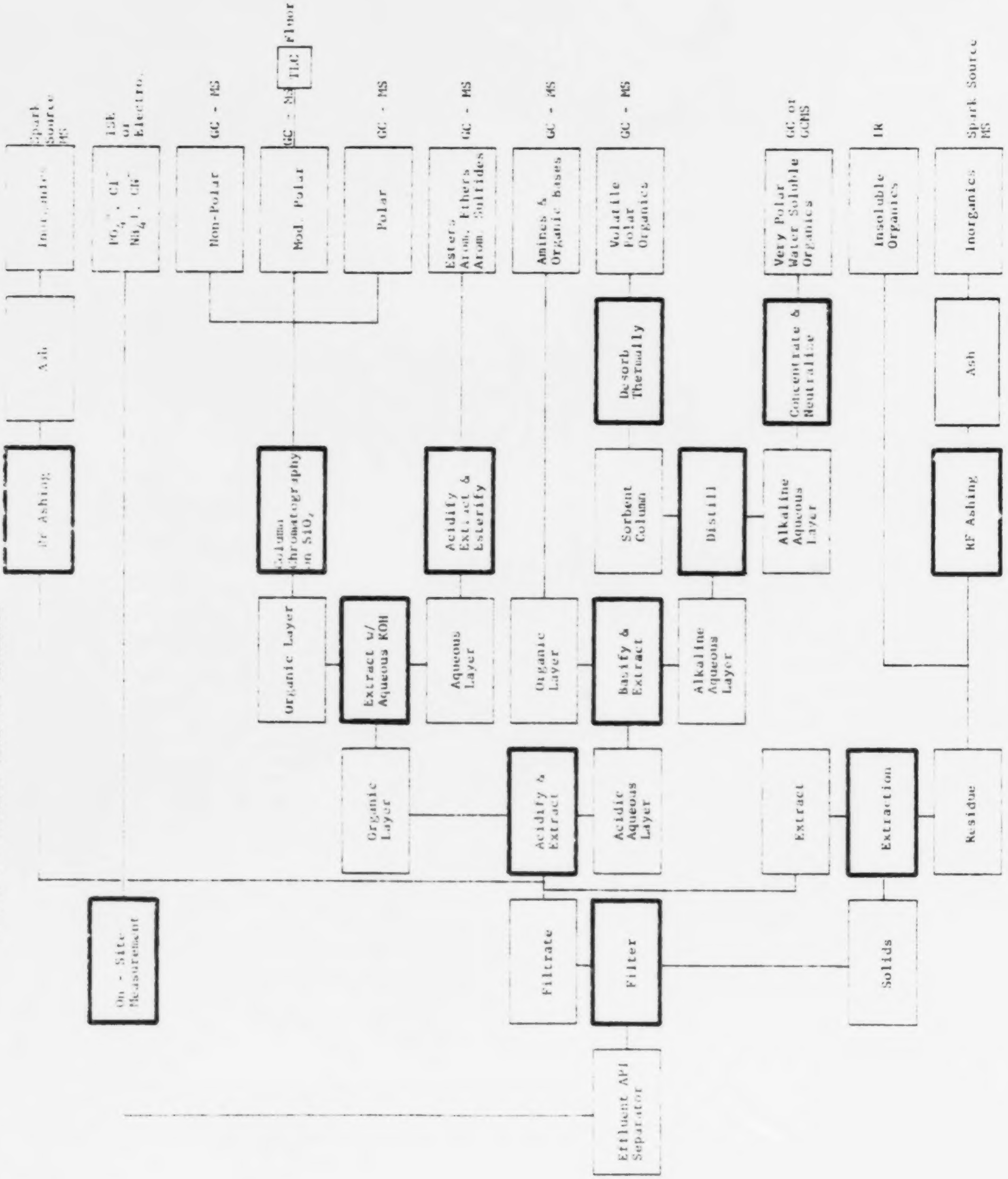
b. If a reference is given, then the compound has been identified as being present. If no reference is given, then the compound is suspected of being present because it was in contact with API separator wastewater within the refinery.

c. Deemed moderately hazardous (see Table A of this appendix).

d. Refer to Volume II, Appendix B, Section 2.2.3 for the complete listing.

FIGURE 2.1-9

STREAM 3 - EFFLUENT FROM API SEPARATOR


Effluent API Separator
Filter
Filtrate
Solids
On - Site Measurement
Acidify & Extract
Organic Layer
Acidic Aqueous Layer
Extract
Extraction
Residue
Extract w/ Aqueous KOH
Organic Layer
Aqueous Layer
Organic Layer
Basify & Extract
Alkaline Aqueous Layer
RF Ashing
Column Chromatography on SiO2
Acidify Extract & Esterify
Sorbent Column
Distill
Alkaline Aqueous Layer
RF Ashing
Ash
Desorb Thermally
Concentrate & Neutralize
Ash
Inorganics
PO4=, Cl-, NH4+, CN-
Non-Polar
Mod. Polar
Polar
Esters, Arom. Ethers, Arom. Sulfides
Amines & Organic Bases
Volatile Polar Organics
Very Polar Water Soluble Organics
Insoluble Organics
Inorganics
Spark Source MS
ISE or Electro.
GC - MS
GC - MS
TLC
Fluor
GC - MS
GC - MS
GC - MS
GC - MS
GC or GCMS
IR
Spark Source MS

The measurement for CN^- is the only one which must be performed on site. A continuous monitor in situ would be preferred but ion specific electrodes for cyanide have strong interference from even a trace of sulfide. Thus, the effluent must be grab sampled and the sulfide interference removed if possible.[1] If the effluent is acidic, the equivalent HCl can be determined as described earlier. Free NH_3 can be performed on site and in situ with an electrode if conditions (pH) indicate the possibility of its presence.

The comments about inorganics and suspended solids for the previous stream are pertinent for this stream. If information concerning the composition of the organic part of the suspended solids is required, the extract of this material can be analyzed separately by the same scheme used for filtrate.

This scheme contains a thin-layer chromatographic separation of the aromatic fraction from the silica gel chromatographic separation. In the absence of a large mass of aromatic hydrocarbons, this separation should be more cost effective than linear elution column chromatography. This decision must be made at decision point 12.

At decision point 6 - before the distillation - the analyst should be aware that, because of the nature of the matrix, further separation of the water solubles is highly desirable and derivatization may be necessary.

---

[1] See Appendix A, Section 1.1.4 for a discussion of this problem.

This sample should be extremely complex because all of the aqueous effluent in the refinery comes through the API separator. For this reason, permethylation is probably desirable at decision point 7.

2.1.2.3 Streams Containing Vapor and Particulate

In streams containing vapors and particulate matter, it is desirable to separate the two phases and to obtain separate analyses on each phase. In addition, the Health Effects Group of the EPA wishes to have particulate matter separated into at least two size fractions, respirable and non-respirable, and to have these fractions analyzed separately. The first requirement increases the complexity of the sampling apparatus and the second requirement increases the sampling time.

The recommended method of sampling these streams is with a modified EPA Method 5 train. Modifications may include inserting specially designed cyclones, replacing impingers with tubes packed with porous polymers and putting reagents other than water in the impingers. The amount of water vapor must, however, be measured. The stack is sampled at a point where mixing is complete and sampling at a point of average velocity should be substituted for traversing the stack. The traverse must be omitted because of the need to use a cyclone for particle sizing, i.e., the variables must be fixed in order for the cyclone to function properly.

If particle size distribution is independently determined either prior to or concurrent with the sampling, the sampling does not have to be performed isokinetically. Some advantage is to be gained if sampling is conducted above isokinetic rates because the collection of smaller particles will be increased in relation to large particles. In general, the limiting time for sampling will be that required to collect a sufficient mass of the small particles.

Sulfur Recovery Unit Tail Gas. At the point of sampling, this stream is primarily composed of nitrogen, oxygen, and water vapor. Probable trace emissions are shown in Table 2.1-8. The amount of water vapor in the stream is a problem when collecting impinger samples or samples in a bottle. The sampling and analysis scheme is presented in Figure 2.1-10.

In-line sample loops will be required because of the high reactivity of sulfur gases such as carbonyl sulfide. The sampling should be intermittent with the sample being used to flush the loop between gas chromatographic analyses. If there are indications that low molecular weight amines are to be found in the effluent, a separate, on-site gas chromatographic analysis should be instituted for them.

A glass sample bottle should be equilibrated at the stack gas temperature and used to collect a sample for light hydrocarbon analysis. The sample bottle should be reequilibrated at stack temperature before the analysis. The analysis should be performed as soon after sampling as possible. In-line loops would also be advisable in this situation, if practical.

The KOH impinger will trap HCN but also all other acidic gases including H_2S. Therefore, the interference from the sulfide ion will have to be removed before CN^- analysis.

TABLE 2.1-8

INCINERATOR TAIL GAS FROM SULFUR RECOVERY UNITS

A. Major Components (Non-Pollutants)

Component	Vol %	TLV (ppm)	Reference
N_2	71.07		GR-145
H_2O	18.57		GR-145
O_2	7.39		GR-145
CO_2	1.45		GR-145
H_2	0.50		GR-145

B. Known to be hazardous and known to be present.

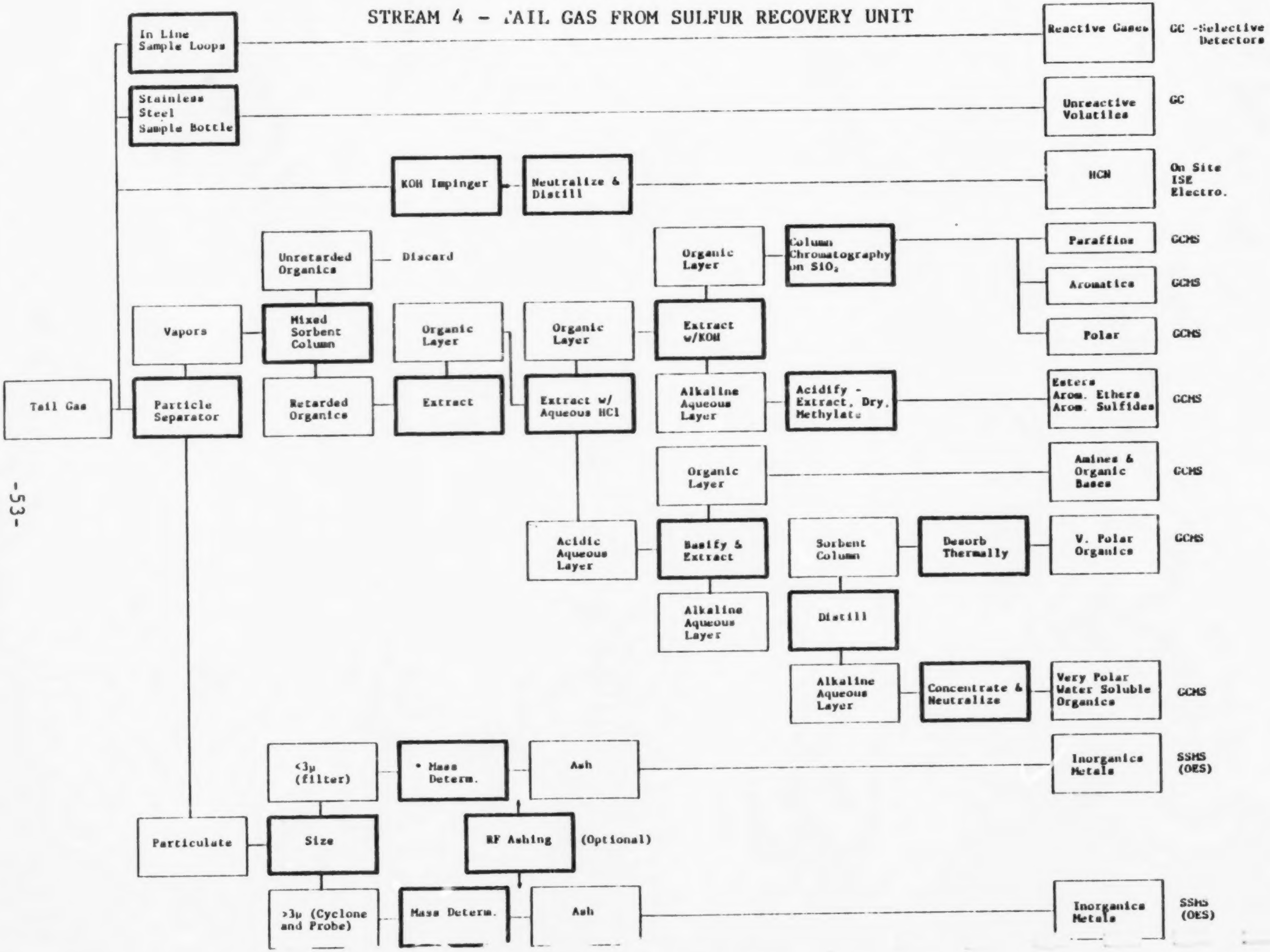
Pollutant	Vol %	TLV (ppm)	Reference
SO_2	0.89	5	GR-145
CO	0.10	50	GR-145
COS	0.02		GR-145
CS_2	0.01	20	GR-145
H_2S	<0.001	10	GR-145

C. Potentially hazardous if present.

Pollutant	Vol %	TLV (ppm)	Reference
C_1-C_4 n-Alkanes	-	500 - 10,000	GR-145, BR-110
Methanethiol	-	0.5	BE-147
Ethanethiol	-	0.5	BE-147
Other Mercaptans	-	-	BE-147
Phenol		5	GO-107, BR-110, BE-147
Cresols		5	GO-107, BE-147
NO		25	DA-069
NO_2		5	DA-069
NH_3		25	ME-107, KL-032
HCN		10	BR-110
HCl		5	PE-140
Monoethanolamine		3	ME-107
Bauxite or Cobalt Molybdate catalyst particulates		5×10^7 particles/ft^3 (Al_2O_3)	BR-110

FIGURE 2.1-10

STREAM 4 - TAIL GAS FROM SULFUR RECOVERY UNIT


Tail Gas
In Line Sample Loops
Stainless Steel Sample Bottle
KOH Impinger
Neutralize & Distill
Particle Separator
Vapors
Mixed Sorbent Column
Unretarded Organics
Discard
Retarded Organics
Extract
Organic Layer
Extract w/ Aqueous HCl
Organic Layer
Acidic Aqueous Layer
Extract w/KOH
Organic Layer
Alkaline Aqueous Layer
Column Chromatography on SiO₂
Acidify - Extract, Dry, Methylate
Organic Layer
Basify & Extract
Alkaline Aqueous Layer
Sorbent Column
Desorb Thermally
Distill
Alkaline Aqueous Layer
Concentrate & Neutralize
Reactive Gases
GC -Selective Detectors
Unreactive Volatiles
GC
HCN
On Site ISE Electro.
Paraffins
GCMS
Aromatics
GCMS
Polar
GCMS
Esters Arom. Ethers Arom. Sulfides
GCMS
Amines & Organic Bases
GCMS
V. Polar Organics
GCMS
Very Polar Water Soluble Organics
GCMS
Particulate
Size
<3μ (filter)
>3μ (Cyclone and Probe)
• Mass Determ.
Mass Determ.
RF Ashing
(Optional)
Ash
Ash
Inorganics Metals
SSMS (OES)
Inorganics Metals
SSMS (OES)

The particulate, in this case, is believed to be free of heavy organics. That supposition is based on the belief that the particulate originally should have no adsorbed heavy organics and it is sampled after coming from an in-stack incinerator. Thus, no extraction of this particulate is planned.

The particulate will be sized into two fractions using a cyclone designed to give a 3μ cut. The two fractions can be weighed and ashed if necessary. The particulate can be analyzed by spark source mass spectrometry for an analysis of total inorganics or can be analyzed only for the suspected bauxite or cobalt molybdate catalyst.

The gases and vapors will be trapped on a porous polymer sorbent. The sorbent may be a mixture such as Chromosorb 101, Chromosorb 105 and Tenax GC, or just Chromosorb 101 and Chromosorb 105 since the suspected components are nearly all acidic or quite volatile. In either case, the adsorbed materials can be desorbed by a solvent extraction with a volatile halocarbon solvent. The extracted components are then separated and analyzed as described in earlier sections.

The major decision points here are numbers 3, 6 and 7. In the case of point 3, the decision involves whether or not to go to a column chromatographic separation or to go directly to gas chromatography - mass spectrometry. This decision could be based on gas chromatography or if sufficient material exists, on infrared. At point 6, the analyst may wish to use gas chromatography or direct inlet mass spectrometry to determine if further separation or even further analysis is required. At point 7, the analyst may use any of the Level I tests for organics to determine if esterification is necessary.

Effluent From the Catalyst Regenerator. The matrix for this stream is similar to that for the previous stream, in that it contains about 20 percent water with the remainder being N_2, O_2, CO_2, and CO. The potential pollutants are shown in Table 2.1-9. The sampling and analysis scheme is presented in Figure 2.1-11.

This is the most comprehensive of the sampling schemes because of the complex nature of the stream. All of the comments about sampling for on-site analysis of the sulfur recovery tail gas are pertinent with two exceptions. First, the temperature of the stream at the sampling point is sufficiently low to use a fluorocarbon polymer lined vessel for obtaining the grab sample. Secondly, the indicated presence of aldehydes in the stream requires another impinger specifically for trapping the aldehyde in a form which will prevent or reduce oxidative degradation. The indicated reagent for the impinger is hydroxylamine which will react with aldehydes to form the corresponding aldoxime. The aldoxime can be chromatographed directly or hydrolyzed back to the aldehyde and chromatographed as indicated. The chromatography should be done on site. Interferences are anticipated from acidic organics. If chromatography of the aldoximes with a nitrogen selective detector is contemplated, the interferences should be minimal.

The particulate sample, being sized into two fractions, generates two extracts to be carried through the separation and analysis procedure. Each size fraction should be treated identically. The extracts are carried through the same separation scheme indicated for the aqueous sample from the API separator. Decisions made at the various points are also similar.

FIGURE 2.1-11

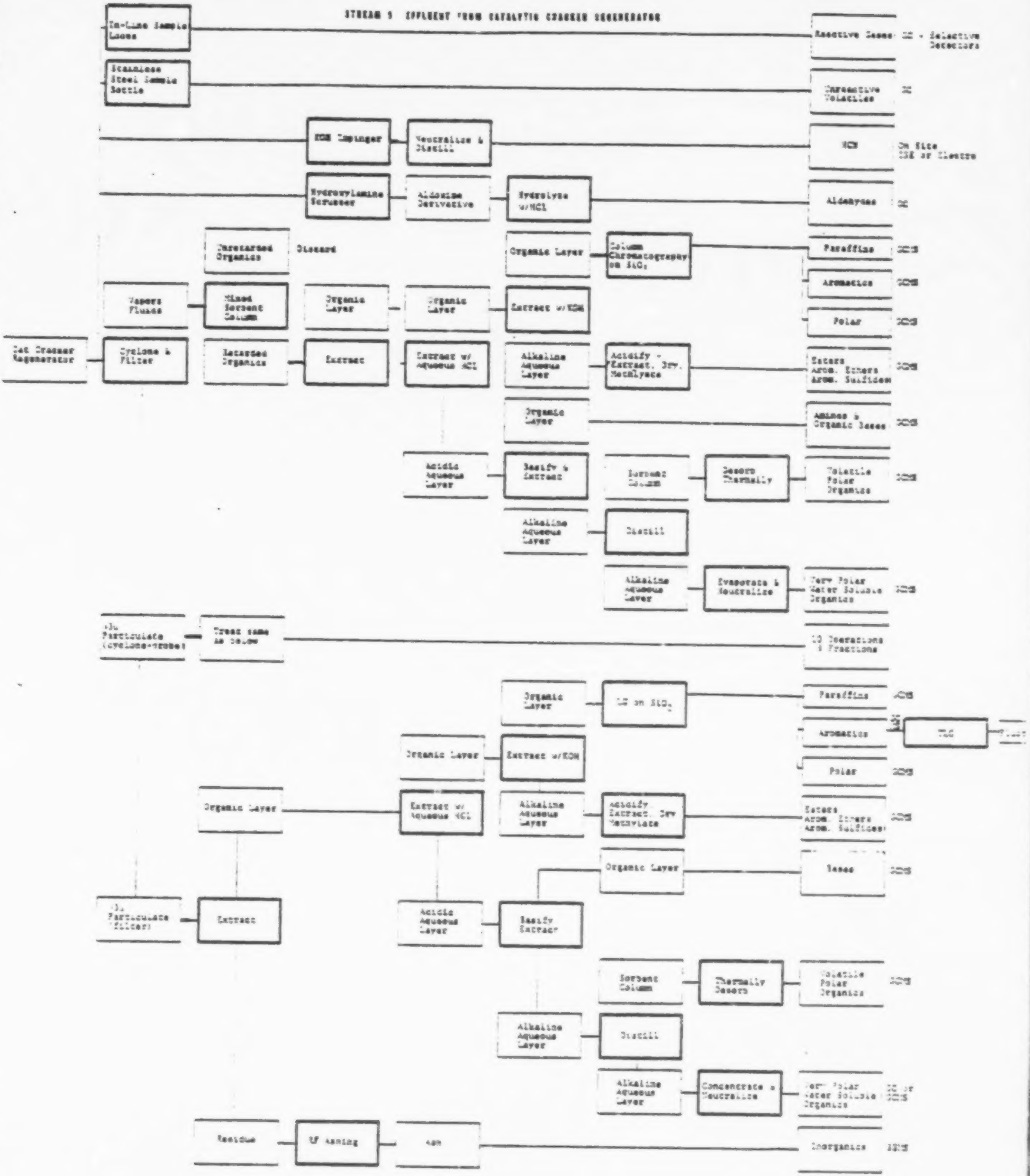

STREAM 5 EFFLUENT FROM CATALYTIC CRACKER REGENERATOR
In-Line Sample Loops
Stainless Steel Sample Bottle
KOH Impinger
Neutralize & Distill
Hydroxylamine Scrubber
Aldoxime Derivative
Hydrolyze w/HCl
Unretarded Organics
Discard
Organic Layer
Column Chromatography on SiO2
Vapors Fluxes
Mixed Sorbent Column
Organic Layer
Organic Layer
Extract w/KOH
Cat Cracker Regenerator
Cyclone & Filter
Retarded Organics
Extract
Extract w/ Aqueous HCl
Alkaline Aqueous Layer
Acidify - Extract, Dry, Methylate
Organic Layer
Acidic Aqueous Layer
Basify & Extract
Sorbent Column
Desorb Thermally
Alkaline Aqueous Layer
Distill
Alkaline Aqueous Layer
Evaporate & Neutralize
Reactive Gases
GC - Selective Detectors
Unreactive Volatiles
GC
HCN
On Site ISE or Electro
Aldehydes
GC
Paraffins
GCMS
Aromatics
GCMS
Polar
GCMS
Esters Arom. Ethers Arom. Sulfides
GCMS
Amines & Organic Bases
GCMS
Volatile Polar Organics
GCMS
Very Polar Water Soluble Organics
GCMS
>3μ Particulate (cyclone-probe)
Treat same as below
LC Operations 3 Fractions
Organic Layer
LC on SiO2
Paraffins
GCMS
Aromatics
TLC
Polar
GCMS
Organic Layer
Extract w/KOH
Organic Layer
Extract w/ Aqueous HCl
Alkaline Aqueous Layer
Acidify, Extract, Dry Methylate
Esters Arom. Ethers Arom. Sulfides
GCMS
Organic Layer
Bases
GCMS
<3μ Particulate (filter)
Extract
Acidic Aqueous Layer
Basify Extract
Sorbent Column
Thermally Desorb
Volatile Polar Organics
GCMS
Alkaline Aqueous Layer
Distill
Alkaline Aqueous Layer
Concentrate & Neutralize
Very Polar Water Soluble Organics
GC or GCMS
Residue
LT Ashing
Ash
Inorganics
SSMS

TABLE 2.1-9

OFF-GAS FROM THE FCCU REGENERATOR

A. Major Components

Components	Vol. %	TLV (ppm)	Reference
CO_2 (dry basis)	7.8-13.4		DA-069
O_2 (dry basis)	2.0-5.1		DA-069
N_2 (dry basis)	80.2-84.6		DA-069
CO (dry basis)	0.0-7.8	50	DA-069
H_2O	18.7-26.3		DA-069
Particulates	0.0174-0.262 [a]		DA-069

B. Known to be hazardous and known to be present.

Pollutant	Concentration (ppm)	TLV (ppm)	Reference
CO	0-78,000	50	DA-069
SO_2	308-2,190	5	DA-069
SO_3	25.6	- [a]	DA-069
COS	9-190	- [a]	RE-142
CS_2	0-2	2	RE-142
H_2S	0-12	10	RE-142
Mercaptans	60-169	0.5	RE-142
Aldehydes (as H_2CO) [c]	3-130	5	DA-069
Cyanides (as HCN)	0.19-0.94	10	DA-069
NO (as NO_2)	8-394	5	DA-069
NO^x	11-310	25	DA-069
NH_3	67-675	25	DA-069
Acetic Acid	∿12	10	DA-069
Anthracene	2,070 [e]	0.1 mg/m^3	HA-011
Pyrenes	40-28,000 [e]	carcinogens	HA-011
Benzo(ghi)-perylenes	15-424 [e]	carcinogens	HA-011
Benzo(a)-pyrene	4-460 [e]	carcinogen	HA-011
Benzo(e)-pyrene	11-3,600 [e]	carcinogen	HA-011
Phenanthrenes	400,000 [e]	carcinogens	HA-011

C. Potentially hazardous if present.

Pollutant	Concentration (ppm)	TLV (ppm)	Reference
C_2 to C_8 n-Alkanes		100-600	HY-013, ME-108
Cyclo Alkanes [c]		300-400	ME-108
1-Hexene		- [d]	ME-108
Benzene		10	ME-108

TABLE 2.1-9 OFF-GAS FROM THE FCCU REGENERATOR (Cont.)
Page 2

C. Potentially hazardous if present. (Cont.)

Pollutant	Concentration (ppm)	TLV (ppm)	Reference
Alkyl Benzenes[c]		25-100	ME-108
Naphthalene		10	HU-114
Biphenyl		0.2	HU-114
Benzofluorenes		carcinogens	TY-008
Benzanthracenes		carcinogens	TY-008
Perylenes		carciongens	HA-011
Phenol		5	ME-108
Cresols		5	ME-108
Alkyl Pyridines		-[d]	LO-112
Quinoline		-[a]	LO-112
Alkyl Quinolines		-[a]	LO-112
Thiophene		-[d]	WO-025
Trace Metals		-[c]	PE-140, AN-104

---

a. Rated as severely hazardous (SA-175).

b. Potentially methanethiol, ethanethiol, and 1- and 2-butanethiol.

c. Refer to Volume II, Appendix B, Section 2.2.5 for the complete listing.

d. Rated as moderately hazardous (SA-175).

e. Micrograms per barrel oil charged (fresh feed plus recycle).

The extremely diverse nature of the compounds in the vapor phase dictates that the mixture of three sorbents should be used in the sampling. It is anticipated that the bulk of the high molecular weight, low volatility compounds will be condensed on the particulate, thus the additional thin-layer chromatographic separation of the vapor phase aromatic fraction from the silica gel step may not be necessary (or there may not be sufficient sample).

The sample should be carried completely through the scheme as shown. The basic decision to be made at any point involves whether or not the separations are sufficiently complete to proceed to the next step.

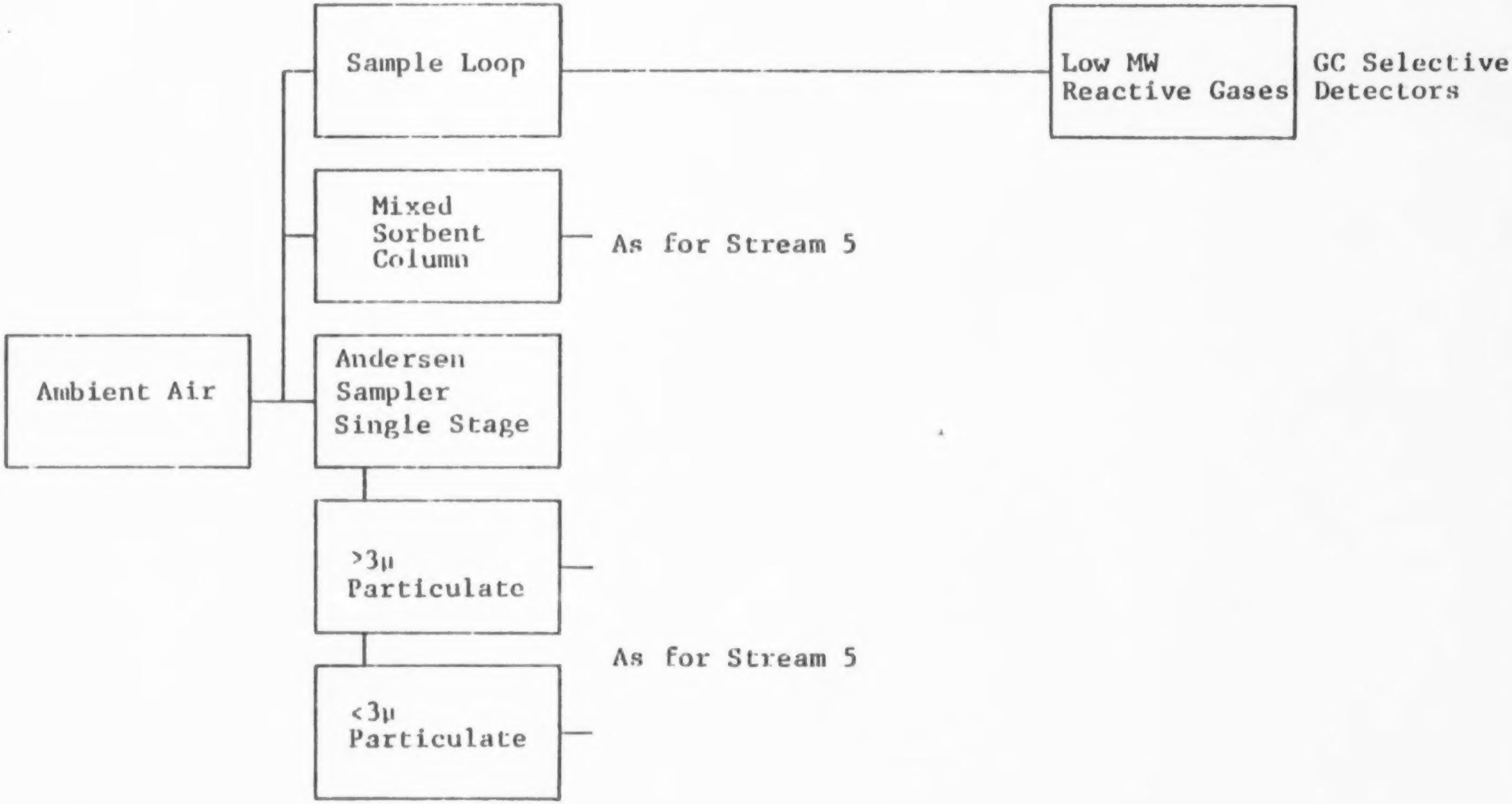
2.1.2.4 Fugitive Emission Samples

The type of samples envisioned in this program are not truly ambient air samples. They are more properly called fugitive emission samples although the mechanics of sampling are similar to ambient sampling. The samples would be collected in an attempt to describe fugitive emissions within a defined area from a defined source. Potential emissions were given in Tables 2.1-1 - 2.1-5. The sampling and analysis scheme is presented in Figure 2.1-12.

In the refinery environment covered by this study, samples would be collected near the atmospheric still and the results should give an indication of the fugitive emissions from the streams discussed in Section 2.1.2.1

Three approaches to sampling can be considered: The first approach is the most complete. It involves designating one station for a background sample and moving the sampling equipment around when the wind shifts. The main sample is a composite of three other sampling stations. A sampling station is located so

FIGURE 2.1-12 **AMBIENT AIR SAMPLES**


Ambient Air
Sample Loop
Low MW Reactive Gases
GC Selective Detectors
Mixed Sorbent Column
As for Stream 5
Andersen Sampler Single Stage
>3μ Particulate
As for Stream 5
<3μ Particulate

as to be as convenient as possible to potential fugitive emissions from the atmospheric still. A sampling station is composed of a Hi-Vol sampler fitted with an Andersen sampling head with a single stage to make a 3μ cut. A separate sampling train containing a sorbent column for vapors will be located near the Hi Vol. The sampling rate for vapors will be at least an order of magnitude less than for particulate. On-station gas chromatographs equipped with sulfur and nitrogen selective detectors will be used to monitor for low molecular weight species. Grab samples in inert gas-bags will be taken and run on site for hydrocarbons. This is the approach which has been costed.

The second approach resembles the first except that all four sampling stations are being used to collect the primary sample. No background sample would be used. This approach substantially reduces both manpower and sampling time requirements and the data may well be just as valuable.

The third approach differs from the second in that no on-station gas chromatography is performed. All gas chromatography is performed on grab samples, on site, but remote from the sampling stations.

The collected particulate fractions and the vapors sorbed on the porous polymers are treated identically to those samples collected from the catalytic cracker regenerator.

2.2 Cost and Manpower Requirements

The costing and manpower requirements for the various sampling and analytical schemes are estimates. The actual costing is extremely site dependent. Matters such as accessibility, distance of travel and locale, available manpower, actual complexity of sample, and company experience can affect these costs and may either raise or lower them. The costs are general, in that the numbers represent an estimate, not from Radian, but of a country-wide average. The start-up costs will be company dependent, varying with the equipment available and the degree of analysis experience relating to a given source. First-time costs always represent the amount of time necessary for an analyst to become familiar with a given type of sample. These costs will vary from source to source.

2.2.1 Basis for Costing

The costing is based on a one-time sampling trip to a refinery to obtain samples from the 5 process streams and a sample which will be indicative of the fugitive emissions from the atmospheric distillation column.

First time costs include: sampling and field analysis equipment; cost of procuring the chemicals for standards; cost of preparing quantitative mixtures for Level III analyses; set-up charges for the laboratory analyses; and, cost of gaining experience in the interpretation of GC-MS data peculiar to a refinery. Subsequent sampling and analysis jobs involving a similar site should reflect a substantial cost benefit derived from the equipment purchased and the experience gained on the first job.

2.2.1.1 Sampling

The sampling will involve 8 men as follows:

5-man team sampling streams 4 and 5 successively,
2-man team sampling the fugitive emissions plus
    streams 1, 2, and 3, and
1 man doing on-site data analysis.

The labor mix for sampling is 50% @ \$20/hour and 50% @ \$30/hour, thus all sampling costs are computed at \$25/hour.

The total sampling effort can be described in terms of its components as shown below. The time spent in actual sampling is long because of the requirement to size the particulate catch and to obtain enough of the smallest size fraction for a complete analysis. It is estimated that 10-15 days may be required to obtain a sufficient sample of the fugitive emissions. Five days at two runs per day may be required to obtain sufficient sample from the catalytic cracker regenerator.

The site is assumed to be located one-day's travel away from the laboratory and thus travel time and direct costs associated with travel become a substantial part of the total sampling cost.

	Days	Men
Travel preparation	5	7
Travel out	1	8
Field set up	2	7
Sampling	10-15	8
Shut down	1	7
Travel back	1	8
Unpack, repair, etc.	5	7

Other direct expenses connected with sampling are:

Travel	$1,600
Subsistence	$6,700-8,200
Expendables (power, reagents, etc.)	$4,700-5,200

Minimum and maximum estimated costs are given based on a variable time required for sample collection. These times are affected by weather and equipment malfunction.

2.2.1.2 Analysis

The analysis costs are made up from the following component costs.

Ion specific electrode measurement	$ 25
Chromotropic acid procedure for formaldehyde	$ 25
Gas chromatographic analysis	$100

Sample preparation

The time estimates include all concentration steps, reagent preparation and purification and minimal special handling.

Sorbent extraction - 1 hour	$ 25
Standard liquid-liquid extractions - 8 hours	$200
Liquid chromatographic separation - 4 hours	$100
Esterification procedure - 1 hour	$ 25

Helium stripping procedure - 1 hour	$ 25

GC-MS Analysis

The use charges for the GC-MS and data system will vary from the standpoint of dollars per hour depending on the specific system being employed, however, the total charge for examining any given fraction should be system independent. The charges do not include the use of any commercial spectral search service because at the present time the cost would be prohibitive.

Charges for the time spent by the personnel who obtain and interpret the spectra are based on the use of a mass spectrometer equivalent to a good quadropole instrument. It is assumed that the operator will be spending part of his time utilizing the library searching or spectral matching capabilities of the data system and that part of the interpretation time will be spent verifying the spectral matches selected by the computer. These cost figures reflect a level of effort for spectral interpretation and presume that major components of interest will be examined. The detection level will be dependent on the efficiency of the separation and concentration steps in the sample preparation procedure and on the elution order from the gas chromatograph. This subject is discussed in more detail in the Appendix.

GC-MS - use charges	$200/fraction
Operator charges - 6 hours	$150/fraction
Interpretation charges - 6-11 hours	$180-330/fraction

Spark source mass spectrometry	$200/fraction

Level I analyses (infrared or spot tests)	$150/sample phase
Expendables (solvents, GC columns, etc.)	$5,000

2.2.1.3 Reporting

Reporting includes all data reduction and compilation, assessments and report preparation plus all report materials. The data from the sampling, calibration, on-site analyses, inorganic analyses and organic analyses will require compilation and reduction to a usable form. The reporting function is the only place in the costing that this exercise has been treated. Assessment, in the context of this report, is the correlation of the reduced data, checks for internal and external consistency, as well as an actual assessment of the existence of problems or hazards connected with the source. Report preparation includes monthly, quarterly and annual reports.

2.2.1.4 Replication

Replication (when desired) applies only to laboratory analyses and is costed the same as the first analysis except that:

> The GC-MS fixed costs and operator costs are reduced because the operating parameters should have been defined during the first pass.
>
> The GC-MS interpretation costs are reduced because now the analyst is primarily concerned with differences between the replicate runs.

GC-MS fixed costs	$100/fraction
GC-MS operator - 2 hours	$ 50/fraction
GC-MS interpretation - 1 hour	$ 30/fraction

2.2.1.5 Start-Up Costs

The various set-up charges for labor can be broken into two categories - charges which are source specific (S) and charges which are completely general (G).

Charges which are source specific are laboratory related. They are intended to cover items such as determining the proper GC columns and associated operating conditions, measuring recoveries in the separation scheme, optimizing MS and GC-MS operating conditions, and familiarizing the interpreter with spectra of model compounds of the primary components. Each of these areas should be covered first in order to reduce the number of errors and the amount of time spent on individual samples.

General charges are those which will only be done once no matter how many different sources will be sampled. The preparation of a van is the largest general charge. The van will be outfitted to be a mobile laboratory and office. It should contain laboratory bench space, sink, hood (optional), small instrumentation and glassware. It must be provided with heating and air conditioning, a source of water, electricity and vacuum (optional).

Sorbent trains (explosion proof)	$ 500/each
Meteorological station	$ 1,000
Intermittent liquid sampler (explosion proof)	$ 1,000
Field GC (for S and N) (explosion proof)	$ 7,000/each
Data loggers for GC's (explosion proof)	$ 3,000/each
"Method 5" particulate trains (explosion proof)	$ 5,000/each
Misc. (ISE meter; sampling bombs; loops for GC's, glassware)	$ 5,000

2.2.1.6 Level III Analyses

The costs below are based on the analysis of samples from each of the streams discussed in this report. These samples will generate between 90 and 100 fractions for GC-MS analysis and 15 fractions for spark source mass spectrometry.

Preparation of quantitative standards 5 man weeks	$ 5,000
Calibrations for quantitative analysis 15 man weeks	$15,000
GC-MS computer charges - for calibration	$ 2,000
Atomic absorption work 12 man hours/fraction	$ 300/fraction
GC-MS additional time - operator 2 hours/fraction	$ 50/fraction

Labor ($25/hour average)

Set-up GC separation for GC-MS	12 man wks	$12,000 (S)
Set-up for sample preparation	4 man wks	$ 4,000 (S)
Set-up GC-MS, operator	5 man wks	$ 5,000 (S)
interpreter	1 man wk	$ 1,000 (S)
use charges		$ 2,000
Van preparation	15 man wks	$15,000 (G)
Set-up for ISE and aldehydes	1 man wk	$ 1,000 (G)
Preparation field GC's (10)	4 man wks	$ 4,000 (G)

Hardware

The hardware cost is not based on specific instruments but rather is a cost calculated to allow purchase of top-quality equipment, and in this case, to allow purchase of explosion-proof equipment wherever possible. There is an unresolved question as to how much homemade explosion proofing will be allowed in many areas of a refinery.

Van	$ 5,000
Van equipment	$ 3,000
Hi Vols (explosion proof)	$ 500/each
Andersens (single stage)	$ 1,000/each

Analysis by GC	$ 75/fraction
GC-MS additional use charge	$ 75/fraction
Additional expendables	$ 2,000
Additional data reduction 2.5 man weeks	$ 2,500

2.2.2 Cost for Comprehensive Sampling & Analysis

	Time	Cost
Sampling		
Labor	190-225 man days	$38,000-$45,000
Expenses		$12,000-$15,000

Analysis

The costs below are based on the analysis of samples from each of the streams discussed in this report. These samples will generate between 90 and 100 fractions for GC-MS analysis and 15 fractions for spark source mass spectrometry.

	Time	Cost
Labor		
Extractions & separations	43 man days	$8,600
GC-MS operation + interpretation	137-202 man days	$28,900-$44,300
GC analysis	8 man days	$1,600
Level I analyses	12 man days	$2,400
Expenses		
Spark source mass spectrometry		$3,000
Expendables		$5,000
Instrument use charges		$19,400
Reporting	200-225 man days	$40,000-$50,000
One Time Start Up		
Labor		$44,000
Hardware	138,000	
Burden @10%	13,800	
	151,800	$151,800
Total One Time Charges		$195,800

	Time	Cost
Replication		
Extraction & separations	43 man days	$8,600
GC-MS operation + interpretation	36 man days	$7,800
GC analysis	8 man days	$1,600
Level I omitted		
Spark source MS		$3,000
Expendables		$2,600
MS use charges		$9,700
	Total Replication	$33,300
Level III Analyses		
Labor		
Calibration	100 man days	$20,000
Sample Analysis	84 man days	$16,800
Data Reduction	13 man days	$ 2,000
	Total for Level III	$50,700

Summary of Costs

Sampling	$50,000-$60,000
Analysis	$68,900-$84,300
Reporting	$40,000-$50,000
Total Level II	$158,900-$194,300
Total Level II with Replication	$192,200-$227,600
Total Level III	$209,600-$245,000
One Time Start-Up Costs	$195,800

Summary of Costs (Cont'd)

Total Level II with Start Up	$354,700-$390,100
Total Level II with Start Up & Replicate	$388,000-$423,400
Total Level III with Start Up	$405,400-$440,800

2.2.3 Basis for Costing - Excluding First Time

		Cost
Sampling	No Change	
Analysis	Separations - no change	$8,600
	GC-MS labor 65-95 man days	$13,700-21,000
	GC analysis	$1,600
	Level I analysis	$2,400
	Spark source mass spectrometry	$3,000
	Expendables	$5,000
	Instrument use charges	$19,400
Reporting	No Change	

The basic changes in costing are: (1) experience in interpretation of mass spectra from refinery samples will allow reduction of time from 4-8 hrs per fraction to 1½-4 hrs per fraction, (2) the cost of a level III analysis will be reduced by the amount of calibration time reagents and use charges required for set up ($23,000), and (3) there will be no sampling or level II analysis set-up charge.

2.2.4 Approximate Cost for Comprehensive Sampling and Analysis of Similar Sites Excluding First Time

Summary

	Cost
Sampling	$50,000-$60,000
Analysis	$53,700-$61,000
Reporting	$35,000-$45,000
Total Level II	$138,700-$166,000
Total Level II with Replicates	$172,000-$199,300
Total Level III	$165,700-$193,700

2.2.5 Cost Basis - Fugitive Emissions Excluded

2.2.5.1 Sampling

If no fugitive emission sample is to be taken, the sampling crew can be cut to 5 men. The sampling time can be reduced to 9-12 days. The set-up time in the field, the travel preparation time, the disassembly time and the travel time will be constant. The time for unpacking, repair, etc., will be reduced. Other direct costs will be reduced proportionately.

	days	man days	cost
Travel preparation	5	25	$5,000
Travel cut	1	5	$1,000
Field set up	2	10	$2,000
Sampling	9-12	45-60	$9,000-$12,000
Take down	1	5	$1,000
Travel back	1	5	$1,000
Unpack, repair, etc.	3	15	$3,000
Other Direct Costs			$8,000-$9,000
			$30,000-$34,000

2.2.5.2 Analysis

By excluding the analysis of the fugitive emission sample the cost of the analyses are proportionately reduced.

	man days	cost
Extractions and separations	27	$5,400
GC-MS	84-126	$18,500-$28,600
GC	5	$1,000
Level I analysis	8	$1,600
Spark source mass spectrometry		$2,200
Expendables		$3,000
Instrument use charge		$12,000
		$45,700-$55,800

2.2.5.3 Reporting

The amount of data generated in the field is substantially reduced. The amount of data generated in the laboratory is reduced by approximately one-third. Thus, even though there remains a substantial task of data reduction and report preparation, the cost should decrease. Estimated costs now are: 150-175 man days - $30,000-$35,000.

2.2.5.4 Replication

Replication costs are proportionately lower due to reduced analyses when fugitive emission sampling is omitted and are computed as before.

	man days	cost
Extractions	19	$3,800
GC-MS	21	$4,800
GC	5	$1,000
Level I omitted		
Spark source mass spectrometry		$2,200
Expendables		$3,000
Instrument use charge		$6,000
		$20,800

2.2.5.5 Start-Up Costs

A major point of concern here is the use of the van. A difference of opinion will easily be found as to the necessity of the van. If no field sampling job larger than that defined herein (without fugitive emissions) is anticipated, the van is probably an unnecessary luxury. However, this report will be based on the probability that larger and more complex sampling is foreseeable.

The start-up costs will be the same as detailed for the entire job except for deducting the following:

	man days	cost
Labor	10	$ 2,000
Hardware		
Hi Vols, Andersons, & Sorbent Trains and met. station		$ 9,000
Field GC's (8)		$80,000
Burden 10%		$ 8,900
		$99,900

2.2.5.6 Level III Analysis

The level III analysis cost is computed as before.

	man days	cost
Fixed Charges	100	$22,000
AA	16.5	$ 3,300
GC-MS	15	$ 3,000
GC	23	$ 4,600
Data Reduction	8	$ 1,600
Expendables		$ 800
GC-MS use charge		$ 4,500
		$39,800

2.2.6 Summary of First Time Costs Without Fugitive Emission Sampling

Sampling	$ 30,000-$34,000
Analysis	$ 45,700-$55,800
Reporting	$ 30,000-$35,000
Total for Level II	$105,700-$124,800
Total Level II with Replication	$126,500-$145,600
Total for Level III	$145,500-$164,600
One Time Start-Up Cost	$95,900
Total Level II with Start-Up	$201,600-$220,700
Total Level II with Start-Up and Replicate	$222,400-$241,500
Total Level III with Start-Up	$241,400-$260,500

2.2.7 Costs for Level I Only

2.2.7.1 Basis

The costing for Level I sampling and analysis presumes that no analysis will be attempted beyond Level I. No provision is made for taking samples which could be used for quantitative analysis and although subsequent qualitative analysis could be attempted, the sample may not be truly representative.

The thesis is that the sample should be put through the separation scheme but no GC-MS analyses will be run and no quantitative data would be obtained other than as a spin-off of spark source mass spectrometry.

No GC analyses will be done on-site. No traverses of stacks will be done. Sample sizes will be much smaller than normally required, thus sampling times will be reduced. Since no on-site GC work will be done, the size of the sampling team will be reduced and hardware costs will be sharply cut. The need for a van is eliminated.

It is estimated that field sampling will still require five men. One man for the one fugitive emission sampler. Three men on the stack sampler and one man taking the liquid samples. In order to get sufficient particulate in the respirable fraction, the sampler should be run for two days on the catalytic cracker regenerator off-gas and the ambient sampler should be run for three days. No fugitive emission background sample will be taken.

The techniques used for the Level I analyses will be infrared, spot tests, high resolution mass spectrometry and spark source mass spectrometry.

Reporting charges will be minimal because there will be little or no data reduction.

Set-up charges will still exist for high resolution mass spectrometry and spot tests. These will be one-time costs.

The cost breakdown is as follows.

2.2.7.2 Sampling

	days	men	cost
Travel Preparation	2	5	$2,000
Travel Out	1	5	$1,000
Field Set-up	1	5	$1,000
Sampling	3-5	5	$3,000-$5,000
Field Take-down	1	5	$1,000
Travel	1	5	$1,000
Unpack, etc.	2	5	$2,000
			$11,000-$13,000
Other Direct Costs			$ 3,000-$4,000
Total Sampling Costs			$14,000-$17,000

2.2.7.3 Analysis

Separations 13 @1.5 man days each	$3,900
Spot tests @$10 each 3/fraction 90 fractions = $2,700 Infrared @$30 each 1/fraction 90 fractions = $2,700	$2,700
High resolution mass spectrometry $500/fraction ($200 labor, $300 MS and computer) Acid, base and neutral fractions only, 13 samples - 3 fractions each	$19,500
Spark source mass spectrometry 13 fractions at $200/fraction	$2,600
Expendables	$1,000
Total Analytical	$29,700

		cost
2.2.7.4	**Reporting** 15-20 man days	\$3,000-\$4,000

2.2.7.5 One-Time Set-Up

Labor - 100 man days (HRMS)	\$20,000
Hardware	
Ambient Sampler	\$ 1,500
Method 5 Train	\$ 5,000
Sorbent Trains -2-	\$ 1,000
Burden @ 10%	800
Total One-Time Charge	\$28,300
Total	\$75,000-\$79,000

Option 1

Depending on the anticipated complexity of the sample, the analyst may opt to obtain high resolution mass spectra without separating the sample into acid, base and neutral fractions. This would change the analysis cost as follows:

High Resolution Mass Spectrometry on sample without separation	\$ 6,500
Separation cost	\$ 0
Infrared = spot tests	\$ 900
Spark source mass spectrometry	\$ 2,600
Expendables	\$ 500

Option 2

In some cases, there may be no need to size the particulate as it is collected. This will lower sampling costs because less time will be expended collecting particulate-bearing samples. In the case under consideration, the analysis costs will be lower, reflecting the fact that there are two fewer samples (one less each from the fugitive emission and the catalytic cracker regenerator).

	Cost
Do Not Size Particulate	
Separation	$ 3,300
Spot tests or IR	$ 2,400
Mass spectrometry	$15,600
Spark source mass spectrometry	$ 2,200
Sampling cost	$12,000-$15,000
Equipment needed under Option 2	
Hi Vol	$ 500
2 Sorbent trains	$1,000
1 Pump and filter train for particulate	$ 500
Burden @10%	$ 200

2.2.8 Summary of Costs (in thousands)

	Total	Opt. 1	Opt. 2	Opt. 1 + 2
Sampling	$14-17	$14-17	$12-15	$12-15
Analysis	29.7	10.5	23.5	7
Reporting	3- 4	3- 4	3- 4	2- 3
TOTAL	$46.7-50.7	$27.5-31.5	$39.5-43.5	$21-25
One Time Costs	$ 28.3	$ 28.3	$ 22.2	$ 22.2
TOTAL	$75-79	$55.8-59.8	$61.7-65.7	$43.2-47.2

As is apparent from the above figures, the cost of Level I sampling and analysis is very much a function of how much information is sufficient.

TABLE 2.2-1

SUMMARY OF COSTS

(in Thousands)

	Comprehensive Program	Program Without Fugitive Emissions	Comprehensive Program After First Time	Level I Program
Sampling	$ 50-60	$ 30-34	$ 50-60	$ 12-17
Qualitative Analysis	69-84	46-56	54-61	7-30
Reporting	40-50	30-35	35-45	2- 4
Minimum Level II	159-194	106-125	139-166	21-51
Replication	33	21	33	-
NORMAL LEVEL II	**192-227**	**127-146**	**172-199**	-
Quantitative Analysis	51	40	27	-
Minimum Level III	210-245	146-165	166-193	-
NORMAL LEVEL III	**243-278**	**167-186**	**199-226**	-
Start-Up	196	96	-	22-28
MAXIMUM LEVEL II Incl. Start-Up and Replication	**388-423**	**223-242**	-	**43-79**
MAXIMUM LEVEL III Incl. Start-Up and Replication	**439-474**	**263-282**	-	-

---

* Level I

TABLE 2.2-2

SUMMARY OF MANPOWER REQUIREMENTS

(in man days)

	Comprehensive Program	Program Without Fugitive Emissions	Comprehensive Program After First Time	Level I Program
Sampling	190-225	110-125	190-225	45-65
Qualitative Analysis	200-260	115-165	130-160	30-65
Reporting	200-225	150-175	200-225	10-20
Minimum Level II	590-710	375-465	520-610	85-150
Replication	90	45	90	-
NORMAL LEVEL II	680-800	420-510	610-700	-
Quantitative Analysis	200	165	100	-
Minimum Level III	790-910	540-630	620-710	-
NORMAL LEVEL III	880-1000	580-674	710-800	-
Start-Up	220	210	-	100
MAXIMUM LEVEL II Incl. Start-Up and Replication	900-1020	630-720	610-700	-
MAXIMUM LEVEL III Incl. Start-Up and Replication	1100-1220	795-885	710-800	0

TABLE 2.2-3

SUMMARY

ESTIMATES OF ELAPSED TIME*

(in work days)

	Comprehensive Program	Program Without Fugitive Emissions	Comprehensive Program After First Time	Level I Program
Sampling	25-30	20-25	25-30	10-15
Qualitative Analysis	50-65	25-50	50-65	15-45
Reporting (Final)	30-40	30-40	30-40	5-10
Minimum Level II	105-135	80-115	105-135	30-70
Replication	40-45	25-30	40-45	-
NORMAL LEVEL II	143-180	105-150	145-180	-
Quantitative Analysis	100-140	70-110	25-50	-
NORMAL LEVEL III	165-230	120-180	165-230	-
Start-Up	40-60	40-60	-	100

NOTE: It is possible that Level II laboratory set-up may go on concurrently with sampling. It is also possible to begin Level III set-up immediately after finishing Level II set-up. Therefore, these times have not been figured into the totals. All above times should be considered to be conservative.

* These estimates are based on the use of a single GC-MS which is often the controlling factor. The estimate also assumes that sufficient trained manpower is available.

2.2.9 Recommendations for Further Work

During the literature reviews, contractor meetings, and reviews with consultants, and as a result of this program, a number of recommendations for further work have emerged. These areas generally deal with field test work, more complete characterization of streams, refinements to fugitive emission sampling techniques, on-site analyses, sensitivity of test methods, and sample preservation.

Field Tests. The general sampling and analytical strategy described in this report should be field tested in a selected refinery. Costs at Levels I, II, and III should also be verified through field testing.

Fugitive Emissions. Fugitive losses represent major emissions from refineries and certain chemical plants, yet the quantity, quality, and environmental effects of these emissions remain poorly defined. Work on methods to accurately determine fugitive emission loss rates in refineries and other process plants is needed. Process operating conditions and general condition of equipment and fittings should be considered prime factors in the study.

More positive sampling and interpretive methods are required. Sampling devices that will assure complete capture of compounds of interest need to be developed. The rationales for locating the sampling equipment need to be established. Means of assuring sample integrity are needed. Ultimately modeling techniques that relate atmospheric emissions to the sources and which correct for background effects will be required.

On-Site Analyses. Although a number of techniques are available for on-site analyses, they are generally either too insensitive, too expensive or too restrictive. Many of the techniques are for inorganic gases or for classes of organic compounds. To our knowledge, no comprehensive list of available methods exists nor are there plans for compiling such a list. This information should be collected and critically reviewed.

Vapor Sample Integrity. A vapor collected on a solid sorber while warm moist air is being drawn over it is not expected to remain stable indefinitely, nor is it expected to undergo the same reactions that it would in the vapor phase in the atmosphere. Materials trapped in impingers also are subject to reaction conditions not encountered in the atmosphere. Positive methods of preserving sample integrity will be required. Work will be needed in this area.

Sample Preservation. Sample preservation is of paramount importance. The compounds of interest may decompose during transport and storage. The fear of decomposition is responsible for much of the costly on-site work. Research is required to determine which samples cannot be preserved and how to preserve those samples which can be returned to the laboratory.

Sensitivity of Test Methods. The available laboratory techniques can generally be applied qualitatively and quantitatively at the sub part per billion level. However, if analytical techniques are not driven to the limits of sensitivity the number of compounds examined per determination will decrease, the costs will decrease substantially, and usually the quality of the results will improve. An optimization study of required information against cost and quality of results would be a useful activity.

Trace Metals. The forms in which trace metals occur in gaseous and aqueous emission streams in refineries are not well known. Work leading to the positive identification of these forms will be required before full assessment of their environmental effects can be made.

APPENDIX A

SAMPLING AND ANALYTICAL TECHNIQUES

APPENDIX A

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APPENDIX A

1.0 INTRODUCTION

Appendix A contains the detailed backup for Section 2.1. Whenever possible the approaches have been referenced to current literature; when this was not possible, inferences were drawn, e.g., a separation possible by gas chromatography is possible by GC-MS.

1.1 Sampling

The sampling strategy is discussed below in terms of the criteria for the sampling devices recommended for this study, the coordinated sampling and on-site analysis work and the preservation of the sample from field to laboratory analysis. Some specific examples have been chosen but these should not be construed to be the only available methods.

Many of the compounds of interest in this paper study or any similar, actual sampling situation will react, in some fashion, if given the proper conditions. Therefore, one of the primary objectives of the sampling strategy is to deliver the sample to the analysis unchanged. Often, the only way to effect this is to conduct the analysis on-site (in situ in some cases).

Because many compounds of interest are present in trace quantities, care must be taken to collect sufficient sample to enable detection of ppb levels of materials. Sufficient sample should be taken to complete all expected analyses from one sampling trip (including some amount of contingencies).

Throughout this report, sampling techniques are drawn from proven state-of-the-art methodology and utilize commercially available equipment.

1.1.1 Sampling Devices

Stack sampling devices should be readily available from commercial sources, although some modifications may be made in order to collect specific samples. The sampling devices should have provisions for collecting and sizing particulate fractions, collecting vapors, measuring water volume and total gas volume, varying flow rate and varying sampling position. In terms of the examples presented in this report, stack sampling equipment should be a modified EPA "Method 5" train (EN-274) as manufactured by RAC, Lear-Siegler and others. High volume stack sampling trains such as that manufactured by Rader (RA-174) may be an acceptable alternative.

Sizing should be done with a properly designed cyclone with the cyclone and filter catches being analysed independently. The cyclone should be designed to make a size cut at 3μ and the sampling systems should be operated at the sampling rate designed for the cyclone. Since a cyclone will only make the desired size fractionation at a specific sampling rate, the process of obtaining a representative sample by traversing the stack should not be used. Instead, preliminary velocity traverses should be conducted and the resulting data used to select an appropriate sampling point. It may be possible to reduce the sampling time considerably if the proper preparations are made for sampling at rates above isokinetic. The preparations for a stack with relatively constant flow and particulate size distribution involve only a preliminary run with an in-stack sizing device such as an Anderson sampler. If the flow and gas properties are subject to variation, concurrent sizing with an independent apparatus may be necessary. By sampling at rates over isokinetic, the catch of fine particulate may be enhanced and since the mass of the fine particulate is generally the governing factor in determining the required collection time, increased sampling rates are very desirable. All sampling equipment must have proper temperature control. Temperature is an important factor because it affects the viscosity of the flue gases and thus affects the operation of the cyclone (LU-013).

Vapor collection should be achieved by proper use of solid sorbents. The solid sorbent should be in a packed column placed in the train after the filter but prior to the impinger train. Proper temperature regulation is required to maintain a temperature low enough to insure good collection efficiency but high enough to prevent appreciable condensation of water in the column. The length of the column and the mass of solid sorbent to be used depend on the temperature and flow rate of the incoming vapors. A check of the literature shows 3" - 5" columns containing from 10 mg to 10 g of sorbent have been used. Modification of the EPA train will be necessary to accommodate the sorbent column and to provide for proper temperature regulation in the sorbent tube compartment.

Impingers in the train are required to trap water vapor and any components of the gas stream which may pass through the sorbent trap. Thus, the water-filled impingers provide a backup trap and the contents should be examined before discarding. (The water probably would not contain any materials which would not also be found in either or both of the acid and alkaline containing impingers, however, the scheduled treatment of the latter may preclude their being examined for spurious compounds.)

Separate probes or separate take-offs from the main sampling probe should be used to collect samples for on-site analyses. The additional probes would be used for the acid impinger, the alkaline impinger, the gold wool, and the impinger for aldehyde collection. Each probe will require individual trains with appropriate pumps, meters, and gauges.

Each of the separate impinger systems will require temperature controls to prevent condensation in the sampling lines and to insure that cooling and water removal is complete in order to protect the pumps. Depending on the point of sampling, some type of particulate removal will be required. This may be accomplished by a plug of glass wool or a filter.

Intermittent sampling of stack gases for on-site analyses should be effected by an automated sampling system on a gas chromatograph. It is anticipated that this system can be installed on the platform at the sampling site or that sampling lines can be run from the sampling point to the gas chromatograph. If more than one gas chromatograph is required, a common probe and sampling line will often suffice. A wide variety of automated process instrumentation is commercially available.

Samples from a potentially variable liquid stream should be taken with a proportional or intermittent sampler. The streams may be homogeneous or heterogeneous and care must be exercised to obtain a representative sample.

In the case of the API separator cited in this report, the sampler must be positioned in a manner which will insure that a representative sample will be collected. This point should be chosen after inspection of the equipment and the site.

Samples from liquid streams which do not have variable compositions may be grab sampled into teflon bottles, stainless steel sampling bombs or collapsed plastic bags contained inside of glass or metal bottles. Pressure reduction devices will be necessary on some streams such as those involving the atmospheric still. Temperature and stream composition are important considerations when selecting a sampling vessel.

1.1.2 Materials Associated with Sampling

The materials of construction are an important consideration in any sampling situation but particularly when a comprehensive analysis is contemplated. The sampler should not interact with the sample to promote reaction by offering catalytic sites or direct chemical reaction. The sampler should be constructed of materials which would not strongly adsorb components of the sample. The sampler should not contribute spurious materials to the sample (i.e., some polymers have a plasticizer bleed).

The sample holder (bottle, filter, etc.) should be thoroughly rinsed or extracted with those solvents that will be used to extract the sample. The solvents themselves must be of the highest quality. Distilled in glass solvents are preferred. The distillation may be performed in the laboratory just prior to use.

The sample probes should be constructed of stainless steel, glass or inert polymer (in increasing order of desirability) depending on the temperatures to be encountered at the sampling point. For temperatures up to 200°C, teflon can be used, between 200°C and 450°C, glass can be used, and above 450°C, stainless steel must be used.

The filters should be high purity quartz fiber rather than fiberglass. Fiberglass and other popular filter media have been shown to contain large amounts of inorganic material (SE-081) and organic materials generally identified as "hydrocarbons." Some filters contain an organic binder and should definitely be avoided because attempting to remove the binder prior to use usually results in decreasing the strength of the glass fiber paper (ME-081). In general, care must be exercised in the handling of all filter media to prevent the introduction of organic impurities during the preparation and use stages of sampling.

Sample collection bottles should be chosen to fit the conditions found in the field (temperature, pressure, and reactivity of the sample stream). A teflon or teflon lined, evacuated, opaque container is preferred.

Sorbents available for vapor collection have a variety of compositions. Charcoal was the accepted sorbent for many years and would function in an aqueous or gaseous environment, however, recovery of sorbed compounds is difficult and generally incomplete (at best). Conventional gas chromatographic coated supports are undesirable because, for our purposes, the sample must be extracted prior to separation and analysis. The preferred sorbents are macroporous resins. The properties and uses of some of these have been reviewed by Dave (DA-148). Some of the resins, such as the XAD series, have been used for sample collection from both aqueous and vapor phases (FR-155)(BU-113). Tenax GC has also been used for both phases (BE-260).

An example of a sorbent column for comprehensive sampling is a mixture of Chromosorb 101 which absorbs and desorbs acidic and neutral components, Chromosorb 105 which absorbs and desorbs low boiling components and Tenax GC which absorbs and desorbs basic, neutral and high boiling components (MI-167). The use of this mixture of sorbents has two primary advantages (1) comprehensive sorbtion, and (2) lowering the cost by "diluting" the expensive Tenax.

The sampling probes used in conjunction with the impingers can be located on the main probe after the filter or can be separate probes of appropriate materials fitted with pre-extracted glass wool plugs or glass fiber filters to remove particulate matter. If small amounts of sample are to be acquired or if the stream is relatively clean, the glass wool plug may suffice.

1.1.3 Fugitive Emissions

The report does not intend to cover ambient sampling. However, the use of ambient sampling devices for collection of fugitive emission samples is intended. In collecting a fugitive sample, we are after emissions from a specific unit or units on a site. The sampling stations should be placed only after intensive site inspection so they have the highest probability of collecting selective fugitive emissions - primarily around valves and pumps and located no more than six feet above grade.

When samples are collected to be measured against a background, one or more samplers should be designated as background and great care must be exercised to keep that sampler upwind from the remaining samplers. A minimum of three other samplers for selective fugitive emissions are recommended.

The particulate sample should be collected using a Hi Vol and the sizing should be done using an Andersen Sampler ahead of the Hi Vol. For the purposes of this study, a single stage with a 3μ cutoff is sufficient (by definition). Sampling should be conducted long enough to collect approximately 1 gram of the < 3μ fraction for the background analysis. Radian and others associated with the program question the value of collecting this sample. Not only is the cost high, but the validity of the data is highly suspect. The major concern is an inability to completely isolate one unit in a refinery and to collect a meaningful background. (One may envision completely enshrouding a unit but this would be far more costly than any approach considered in this report.) The sampling times considered in the body of this report are very conservative and depend on the following factors: (1) a particulate loading of 75 ug/m^3; (2) a sampling rate of 1 m^3/min (35 cfm); (3) sampling 24 hrs/day for 10 days; and (4) at least 25% of the particulate to be below a 3µ size. The above factors allow

$$\frac{75\ \text{ug}}{1\ \text{m}^3} \times \frac{1\ \text{m}^3}{1\ \text{min}} \times \frac{60\ \text{min}}{1\ \text{hr}} \times \frac{24\ \text{hrs}}{1\ \text{day}} \times 10\ \text{days} \times \frac{.25\ \text{ug} < 3\mu}{1\ \text{ug}}$$
$$= .27 \times 10^6 \text{ug} < 3\mu$$

Thus, even if it were possible to sample 24 hrs/day, the whole approach depends on a heavy particulate loading and good size distribution just to obtain about 25% of the required amount of background sample. The likelihood of being able to sample a true background consecutively for 24 hrs is small and for 10 days is nonexistent.

If the background sample is omitted, this unit can be moved into the area with the other three samplers. The sampling time should thus be reduced by at least a factor of four because four filter catches are now being pooled and the samplers can run continuously rather than being stopped intermittently while the background sampler is repositioned. As the above calculation shows, four samplers could provide enough sample if everything went perfectly, however, another factor must be considered. The sample will be strongly influenced by the emissions from other units in the area and an accurate assessment of the emissions from the desired unit would be impossible, and indeed, the data may be misleading.

Sorbers should be used to collect vapors and gases from the air. The mixed bed three component sorber is an example of what can be used. The sorbent columns should be fitted on separate sampling trains because they would cause too much pressure drop on the Hi Vol's. Flow rates of 1-2 liters/min should give good retention by the sorber and not cause too much pressure drop (MI-167).

The sorbent samplers should be used throughout the Hi Vol sampling time. This means extremely long sampling times during which two things can occur: (1) many volatile compounds may be displaced from the sorbent, and (2) high volumes of air being drawn across the condensed materials will probably cause oxidative reactions not found in the gas phase, i.e., sample integrity becomes highly suspect.

1.1.4 On-Site Analyses and Associated Sampling

Because of the controversy surrounding sample preservation, some analyses should be done on-site, in situ, if possible. It has been stated that most low molecular weight sulfur gases (AM-066)(HI-116), low molecular weight nitrogen compounds (BE-088), and aldehydes (NO-070) are reactive and should be analyzed as soon as possible after collection. Other materials such as KCN have a limited stability (ST-277) and hydrocarbons are believed to become strongly adsorbed to the walls of the collection vessel (TE-205).

Analyses which are to be performed on site should be rapid and simple. The techniques and equipment should be capable of analyzing for more than one compound at a time (which makes gas chromatography a prominent candidate) and should be as free from interference as possible.

In the specific case of the refinery, the following recommendations are made:

The low molecular weight sulfur gases such as CS_2, COS, H_2S, methyl-butyl mercaptans and dimethyl sulfide should be collected in in-line sampling loops. The sampling loops should be of a fluorocarbon polymeric material, such as teflon. The lines and associated gas chromatographic components should also be of a tefon-like material. These compounds can be detected using a flame photometric detector with an interference filter passing the sulfur emissions. The separation of these compounds is often effected on glass columns packed with phosphate esters on a variety of supports (KR-062),(OK-014).

H_2S, COS, CS_2, and SO_2 have also been successfully analyzed on deactigel (TH-094) and Porapak Q (BA-315),(HE-113). When ppb levels of the sulfur compojnds were anticipated, the analysis has been conducted using polyphenyl ether 5 ring polymer with H_3PO_4 on powdered teflon (ST-007).

Low molecular weight amines should also be analyzed with a selective detector - either a Hall conductivity detector or a coulimetric detector. Typically, carbowax columns are used for this separation, e.g., (SM-096). In-line sample loops are recommended but as an alternative, H_2SO_4 impregnated glass fiber filters have been used to trap the amines. Desorption and gas chromatography on 15% diglycerol plus 5% tetraethylene pentamine plus 2% KOH has been shown to give 100% recovery at sampling rates up to 15 l per min (OK-014).

Aldehydes are easily oxidized and should be trapped in a separate impinger containing bisulfite (IN-061) or hydrooxylamine hydrochloride (NO-070). The bisulfite adducts can be determined by gas chromatography on 15% carbowax 20 M on chromosorb followed by dinonylphthalate on fire brick. Detection limits are ∿50 ppb for a sample of 60 l. Sampling rate is 2 l/min. Formaldehyde can be determined on an aliquot by the chromotropic acid method (LE-190). The detection limits again are ∿50 ppb. Acrolein can also be determined colorimetrically on a sample aliquot. The detection limit for acrolein is ∿200 ppb (FE-104)

HCN can be collected in an impinger containing aqueous KOH. The impinger will also collect other acidic gases and one of these - H_2S - poses a serious interference to the determination of CN^-. The CN^- can be determined by ion selective electrode in the absence of $S^=$ and after distillation of HCN. In the absence of $S^=$, it can also be determined by colorimetry. There is no commonly used measurement technique for CN^- which is not subject to interference from $S^=$ with the exception of gas chromatography. The use of solid sorbents to trap the distilled HCN followed by thermal stripping in the injection port is a possible analysis tool. Selective detectors for nitrogen may be used if necessary. Solutions of KCN in water decompose rapidly, so analyses should be made as soon as possible.

Many researchers have found it expedient to analyze bomb samples of low molecular weight hydrocarbons in the field and that is recommended for this study. The analysis can be performed by gas chromatography using a flame ionization detector. Many columns are recommended for the C_1- C_5 hydrocarbons, among them various loadings of dimethylsulfolane on a variety of supports (CS-008) and Porapak Q (WA-188). The Porapak Q column is recommended for this study.

Mercury poses a particular problem in sampling because its volatility as an element and because of the volatility of many of its organic derivatives. A separate train will be required.

The train should contain gold wool which will absorb Hg vapor, inorganic Hg and organomercury compounds (LE-017). After desorption, the mercury may be determined by atomic absorption.

1.2 Separations

The separations recommended in this report involve extractions from particulate and porous polymer sorbers, liquid-liquid partitioning, liquid chromatography, distillation and He stripping. The function of the separations is to prepare the fractions for qualitative and quantitative analyses which may in themselves involve further, more sophisticated separations.

1.2.1 Extraction

Extractions from particulate and solid sorbers are similar in principle. The solvent of choice must be as pure as possible and laboratory purification of commercial products may be required. The solvent should be volatile so that it can be concentrated with relative ease. Depending on the class of compounds expected in a given sample, the solvents for extraction may be chloroform, dichloromethane, freons, diethyl ether, benzene, pentane or methanol or combinations of ether or methanol with the other solvents. The extraction may be carried out in a Soxhlet extractor or similar device or on a fritted filter. In general, it is wise to use as little solvent as is required for the extraction in order to hold down the necessary concentration factor.

The extractions involved in the specific problems discussed in this report should use dichloromethane or freon. Studies in the EPA laboratories at Athens, Georgia have shown that $CHC\ell_3$ is the best solvent for extracting organics from water samples (KE-156). If the analyst suspects that extraction is not complete with those solvents he should reextract with another solvent and examine the second extract with GC or infrared (if possible). If additional extraction has occurred with the second solvent, the solvents should be combined and carried through the separation scheme.

The use of a Soxhlet or Soxhlet type of device is recommended. Overly long extractions should be avoided. The extracted material should be retained until its exhaustive extraction is confirmed. A blank should always be carried through the procedure. Polynuclear aromatics can be selectively extracted from particulates by using DMSO and reduced pressure in a Soxhlet type of apparatus (NA-247). Reduced pressure during extractions also facilitates the use of many other high boiling solvents should they be necessary.

In general, all extractions should be performed at as low a temperature as possible in order to avoid sample loss through volatization or thermal decomposition. If extractions are incomplete at low temperatures, it is recommended that the analyst seek other solvents rather than heat the sample.

1.2.2 Liquid-Liquid Partitioning

Liquid-liquid partitioning involves moving a selected material or materials from one liquid phase to another. Partitioning, as it is envisioned for the overall separation scheme, involves separation of the mixture of compounds on the basis of their acid and base character.

There are several problems involved with this approach but none of the alternatives seem more attractive. The problems involve: (1) distribution coefficients; (2) large volumes of solvents; (3) impurities introduced by reagents; and (4) acid or base catalyzed reactions.

Distribution coefficients will be less of a problem in the first step which removes basic compounds because the volumes of the two liquids may be nearly equal before the sample carrying phase is diluted with the wash liquid. When the volumes are equal, distribution coefficients as low as 1.0 will still give 94% recovery with four passes. However, if the sample carrying phase has five times the volume of the extracting phase, the distribution coefficient must be five in order to achieve the same degree of separation. This emphasizes that when working for good recoveries in a comprehensive analysis of total unknowns several extractions will be necessary to guarantee the separation. If separation cannot be effected with four passes a different solvent or a different technique should be employed. When the volume of solvent carrying the sample becomes large, the analyst must concentrate that phase or be faced with using larger and larger extractant volumes.

When proper technique is used the volume of the sample-carrying solvent increases as it passes along through the separation scheme because the various extracting solutions should be washed with the primary solvent and this wash solution added to the sample solution. As discussed below, it may become necessary to concentrate the sample during the separation procedure.

Purity of reagents is of utmost importance in liquid-liquid partitioning. Trace impurities soon become concentrated and may indeed hinder the analysis for trace components of the sample. If inorgani analysis for trace metals is contemplated, this analysis shoul be performed on a portion of the sample which has not been exposed to acids or bases.

Materials such as indoles and carbazoles are known to undergo acid catalyzed polymerizations (HA-331). The only recourse the analyst has is to perform the extraction and remove the extracted material from the catalyzing phase as soon as possible. There are several other examples of acid or base catalyzed reactions, including the condensation of phenols and aldehydes and the aldol-type condensation of aldehydes (NO-070), (SN-027).

Other types of separation schemes involving ion exchange resins or distillations are even less desirable than liquid-liquid partitioning. Acid ion exchange resins, for example, take out some nitrogen heterocyclics, catalyze the polymerization of indoles and carbazoles and remove some polynuclear aromatics (MC-141). Distillation as a means of separation generally requires acid or base to be added to the pot and thus promotes oxidation and chemical reactions even more than liquid-liquid partitioning because of the elevated temperatures. In spite of the problems with distillation, it is recommended at one point in the analytical strategy for lack of a better, proven method of separation.

Most samples will have some very polar compounds which will remain in the first aqueous layer contacted. For example, formic acid will be extracted out of a nonaqueous phase by aqueous acid as will methanol, glycols, methylamine, and zwitterionic materials. These will not be found in the generally expected fraction based on their acid and base properties. Consequently after the aqueous acid phase is basified and organic bases extracted away the aqueous phase must be retained and analyzed for very polar materials.

Analysis of raw aqueous samples may give some singular problems. For example, after proceeding through the liquid-

liquid partitioning, as much as 90% of the total organics may remain in the water phase (GA-145).

At the conclusion of liquid-liquid partitioning, the fractions containing the separated components must be concentrated. The volumes which may be on the order of several hundred milliliters must often be reduced to one ml or less. Several techniques are available for this including a reduced pressure rotary evaporator, a Kaderna-Danish evaporator, freeze drying, and evaporation under a stream of inert gas (WE-158). The utility of these techniques depends on the solvent and the suspected volatility of the components.

In general, for the type of components found in the example used for this report, HCl and KOH will be the acid and base used as reagents in the partitioning. These will enable the analyst to reach any practical pH extremes. If the solution must be retained for trace metals analysis and if pH extremes are not required, pH adjustments may be made by distilling HCl or NH_3 vapors into the sample. (Redistilled HCl and NH_4OH may be used if they have been stored in teflon bottles.)

In some instances, such as the removal of acidic compounds from the aqueous layer, the analyst may wish to add large amounts of inorganic salts to help shift the distribution to the organic phase.

1.2.3 Column Chromatography

Three types of column chromatography are proposed for use in this scheme: (1) non linear elution chromatography; (2) linear elution chromatography, and (3) reversed phase chromatography.

The most popular column chromatographic technique is non linear elution chromatography (CC). This is generally used to prepare three fractions; non polar or aliphatic hydrocarbons; moderately polar or aromatic hydrocarbons and sulfides; and polar or oxygen and nitrogen containing components (NE-111). Silica gel (SiO_2) and alumina (Al_2O_3) are the usual supports although cellulose, acetylated cellulose and many others have been used (SN-026). Silica has been shown to have a much smaller retention volume than alumina for multiringed aromatics (SN-028) and thus is the sorbent of choice for the samples in this report.

Any sorbent's retention properties are dependent on its degree of activation. The more activity a sorbent possesses the more retentive it becomes. In normal use silica is deactivated with between 1 and 5 weight percent water. Calcined alumina has also been extensively used and has been shown to give 100% recovery and separation of saturates from unsaturates (SN-027). The eluting solvents for silica gel may be a series such as pentane followed by chloroform and finally methanol. The eluting solvents for alumina are pentane followed by diethyl ether and finally 50/50 benzene methanol (SN-027).

Linear elution chromatography (LEC) is generally performed on alumina containing 0.4 - 4.0 percent water. Sample size is much smaller than for CC but separation between fractions by ring size is excellent and recoveries approach 100%. A variety of eluting solvents have been used, among them pentane, 25% benzene in pentane, 50% diethyl ether in pentane and finally 50/50 benzene-methanol (SN-023). Sulfur compounds elute with the aromatics and are not separated by the LEC described above. If such a separation is desirable the entire aromatic fraction from the silica gel LC can be treated as described in the Bureau of Mines Report on sulfur compounds in crude oil (RA-175). For purposes of the examples in this report, LEC is probably necessary only for the aromatic fractions from CC of the gas oil and topped crude. Reported recoveries are generally greater than 95% and always greater than 85% even when μ gram quantities are involved (SN-030).

Reversed phase chromatography is column chromatography performed on a non polar support with polar eluting solvents. The only use currently envisioned for this technique is for further separation of the polar phase from CC of the gas oil and topped crude samples. Solvents are generally mixtures of water and alcohol or water and acetonitrile while sorbents are usually porous polymers. Excellent separations of nitrogen and oxygen containing aromatics have been accomplished (SC-256).

1.2.4 Distillation

In order to achieve further separation of the water soluble organics, a distillation step has been proposed. If the aqueous solution is alkaline, all compounds which are salt-formers under these conditions will remain in the pot. The distillation will then remove many of the basic and neutral compounds. The distillation may be conducted in one or two steps and may give 10 - 1000 fold concentration factors (GA-145). This distillate may be trapped on a sorbent or collected for direct aqueous injection for GC-MS.

1.2.5 Helium Stripping

Generally speaking it is only feasible to helium strip compounds with boiling points lower than 150°C and then recovery may be poor, averaging between 40% and 50% (NO-067). However, this may be a practical way to separate volatile organics from the original sample before solvent partitioning.

The compounds would be stripped for 30 to 60 minutes and adsorbed on Tenax GC or other suitable sorbent. Low flow rates and small amounts of sample should insure their retention by the sorbent. The compounds can be removed from the sorbent by thermal means and inlet directly to a general purpose gas chromatographic column for analysis.

1.2.6 Derivatization

There are many points in the separation scheme where derivatization may be desirable. One of these (the acidic compounds) has been indicated. Other fractions where derivatization may potentially be desirable include: the two water soluble fractions, the alkaline compounds, and the polar cut of the neutrals fraction.

Many derivatizing agents are available but, except for those which methylate the compound, all suffer from an identical problem. The spectra of the derivatives are not usually found in standard compilations of mass spectral data. Many methylating agents are available, among these are diazomethane, BF_3- methanol, dimethyl sulfate, and "on-column" reagents. A discussion of the usefulness of the various methylating reagents is contained in WE-158.

1.3 Distribution of Compounds

In general, application of the recommended separation scheme will result in the following distribution of compounds:

1. Acidic Aqueous Extract - Water soluble polar organics and compounds with basic character such as amines, some imines, and tertiary amides.

- 1A. Extract of basified solution 1 - organics with basic character
- 1B. Extracted basified solution 1- water soluble polar organics
- 1BA. Sorbent for distilled volatile polar organics
- 1BB. Stripped basified solution 1 - low molecular weight acids, zwitterions, other water solubles

2. Alkaline Aqueous Extract - organic acids both carboxylic and sulfonic, pyroles, phenols, thiols, primary and secondary nitro compounds and imides
   - 2A. Methylated organic extract of solution 2 - esters, anisoles, sulfides, imides, nitro compounds, and pyrroles*
3. Neutral Organic Fraction - all hydrocarbons, most nitrogen, oxygen and sulfur heterocyclics, sulfides, and other sulfur compounds, carbonyls, ethers, esters, nitriles, some nitrated and halogenated compounds and a variety of other neutral species.
   - 3A. Non polar cut from SiO_2 - aliphatic hydrocarbons
   - 3B. Moderately polar cut from SiO_2 - aromatic hydrocarbons, some olefins and sulfides

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* If desirable this group can now be further separated by reextracting with an alkaline solution - esters, ansioles and sulfides do not extract but care must be taken not to hydrolyze the esters.

3C. Polar cut from SiO_2 - all other neutral compounds

Using the above numbering system, it is possible to predict the distribution of the hazardous pollutants in the streams cited in this report. For example, for the sample from the catalytic cracker regenerator off gas the distribution would be as follows:

Solution 1A - pyridine, alkyl pyridines, quinoline and alkyl quinolines

Solution 1BA - methanol

Solution 1BB - formic acid and acetic acid

Solution 2 - phenol and cresols, methanethiol, ethenethiol, 1-butanethiol and 2-butanethiol

Solution 3A - n-pentane, n-hexane and decalin

Solution 3B - all polycyclic aromatic hydrocarbons, benzene, alkyl benzenes, tetrahydro naphthalene and thiophene

Measured On Site - C_1-C_5 hydrocarbons, acetaldehyde, CO, SO_2, CO_2, NO, NO_x, NH_3, HCN, SO_3, COS, CS_2, H_2S, HCl, and C_1-C_4 thiols.

1.4 Level I Analyses

Level I type of testing can be applied to any sample regardless of the method of collection. Its use is intended only as a screening tool. Applied to samples collected expressly for that purpose, it has as much revelance as when applied to samples collected for Level III analysis. Except in a few specific instances, the Level I analyses will not be a good indicator for trace compounds. These cases are indicated later in this section.

A Level I type of testing can be extremely valuable if it is used during the separation scheme to help the analyst make decisions. Used in that context, the analyst can decide which solutions to further separate, which solutions to qualitatively analyze and whether or not his separation techniques have achieved the desired result.

The available techniques are direct inlet low and high resolution mass spectrometry, microscopy, infrared spectroscopy, ultraviolet spectroscopy, gas chromatography, and functional group spot tests.

Direct inlet, low resolution mass spectrometry can be used for samples suspected to contain compounds which are solids or high boiling viscous liquids at standard conditions. Experimentally, the sample is introduced to the mass spectrometer and the temperature is slowly increased. The desired mass range is scanned when indicated by changes in the total ion current. The mass spectrometer may be operated in the electron impact or chemical ionization mode. Low voltage electron impact mass spectrometry should supply the most usable information. If 12 - 15 ev ionizing voltages are used, the mass spectra will be more oriented toward molecular ions and much less cluttered by fragment ions, thus, the screening function will be better served. Chemical ionization spectra may also be obtained at low voltages, however, the data may be harder to interpret than electron impact data.

When used for Level II screening, it may be necessary to discriminate which data will be interpreted. Discrimination may be on the basis of relative intensity of peaks, mass or a combination of both. The sensitivity will be on the order of parts per million (higher for volatile compounds which flash off and lower for very non volatile compounds). It is, however, a destructive technique and may produce more information than can be interpreted so the analyst must be alert to the danger of spending too much time trying to interpret the spectra.

Direct inlet high resolution mass spectrometry is utilized in the same fashion as the low resolution technique. The sensitivity is not as high, the sample consumption is greater than in low resolution, and temperatures are not normally varied. However, the amount of information gained can be quite large because of the ability to get precise molecular weight information. The utility of this technique is greatest when analyzing for a preselected list of compounds for which a matrix of ions has been prepared. When operating with a highly computerized system and a preselected matrix, the probable presence or certain absence of compounds on the list can be established at the operating level of the instrument. Low voltage scans would be recommended in order to keep the total number of ions down. The sensitivity will be inversely proportional to the resolution and to the volatility of the compounds.

Microscopy finds its primary use in the examination of particulate matter. Using this technique the analyst may gain limited insight into the effectiveness of the extractions or the amount of organic material associated with particulates. The technique is rapid and nondestructive, but only in the hands of highly trained personnel. The ultimate utilization of microscopy involves the electron microscope in conjunction with an x-ray microprobe for inorganic analysis.

Infrared spectroscopy would seem to be particularly valuable at Level I for several applications. Solutions may be scanned for completeness of separations and for the presence or absence of various functional groups. In its normal application, the technique is nondestructive and rapid, however, it is somewhat insensitive (milligrams of compound per scan) and subject to interferences from the matrix. Problems with the matrix include, for example: the interference of a water matrix with monitoring of hydroxyl or amino bands as well as the need for an inert cell; and, the interference of major aromatic components (low molecular weight) with minor but important components (polynuclear aromatics). Modifications of the basic technique such as attenuated total reflectance (ATR) infrared or Fourier transform infrared (FTIR) greatly increase the sensitivity (micrograms of compound per scan) but matrix effects are still a problem.

Ultraviolet spectroscopy does have some applications at Level I. These are in monitoring effluents from LC columns and determining the amount of aromaticity in various fractions. The technique is intermediate in sensitivity (submilligram to micrograms of compounds in a cell), rapid and nondestructive, however, its utility is limited.

Spot tests have general application throughout the separation scheme. The tests are normally specific for classes or functional groups. The amount of interference varies from test to test but can usually be minimized. The tests are sensitive (microgram to submicrograms of compounds spotted), and rapid but destructive. Spot tests exist for almost every known functional group or combination of functional groups (FI-085).

1.5 Level II Analyses

Although, by definition, Level II testing should be qualitative there are many occasions where semiquantitative information is available as fallout data. These instances will be discussed under the specific techniques.

The techniques available for Level II analyses are high resolution mass spectrometry (HRMS), gas chromatography-mass spectrometry (GC-MS), gas chromatography (GC), high-pressure liquid chromatography (HPLC), paper chromatography (PC), thin layer chromatography (TLC), fluorescence spectrometry, ultraviolet spectrometry, spark source-mass spectrometry (SSMS), optical emission spectrometry (OES), x-ray fluorescense spectrometry (XRF), and ion selective electrodes. The existence of many other techniques in the desired sensitivity range (microgram and submicrogram) is acknowledged but these will not be discussed.

High resolution mass spectrometry is valuable because accurate mass determinations will often identify compounds definitively if mixtures are not too complex. As described under Level I, the primary value of high resolution mass spectrometry is for determining possible presence or certain absence of preselected compounds.

When sufficient sample is available, a gas chromatography-high resolution mass spectrometry combination may be used for confirmation of low resolution GC-MS data.

A resolution of approximately 15,000 will be sufficient for most studies. To achieve high sensitivity, GC-MS photo plate detection is almost certainly necessary. (This topic is thoroughly covered in reference MC-166.) High resolution, with a photo plate, can be accomplished if 66 ng of compound are injected into a GC and give a peak 20 seconds wide. This is approximately 300x better than can be done with electrical detection (CO-316).

The technique cannot differentiate between isomers and often cannot offer information for differentiating between compounds of iso atomic structures (e.g., diethyl sulfide, methyl propyl sulfide, and butyl mercaptan) if the matrix is complex.

Gas chromatography-mass spectrometry combines separation and identification and is perhaps the single, most powerful tool available to the analyst. Compounds can be identified based on both their mass spectra and their GC retention time. A variety of options are available for GC-MS, including: the use of low ionizing voltage; chemical ionization; specific ion monitoring; and a variety of GC columns.

Low ionizing voltage (12 - 15 ev) generally simplifies a mass spectrum by reducing the number of fragment ions formed. However, most of the spectra stored in the files for computer searching were obtained at 70 ev and will not be comparable with low voltage spectra.

Chemical ionization spectra show greatly enhanced quasi molecular ions (M+1 or M-1) which give great insight into the molecular weight of a compound. In many cases, the reactant gas can be used as a carrier gas in GC-MS. Again, the spectra are not amenable to computerized spectral matching because the available files contain primarily high energy electron impact spectra. Chemical ionization spectra are best used along with electron impact spectra as additional information.

Specific ion monitoring (SIM) can be of great importance in GC-MS work. Most modern instruments (particularly quadrapole spectrometers) can monitor between 1 and 6 or 8 selected ions simultaneously. The operator can use this technique very advantageously when the background is high, only small amounts of sample are available or when only a few compound types are of interest. It has been found that use of SIM techniques give sensitivities about two orders of magnitude better than total ion monitoring techniques (MI-175) which can result in the detection of subnonogram quantities per GC injection.

The analyst has a variety of GC columns available to him. The column selection is influenced by a requirement to keep the column bleed as low as possible. Thus, chemically bonded or support bonded liquid phases are desirable, as are thermally stable porous polymers such as Texax GC. (The lower the background-the higher the sensitivity which can be realistically achieved.) The analyst may also select from capillary columns, SCOT columns or packed columns. Capillary columns give excellent resolution but require that only small samples be used. Packed columns sacrifice resolution but may handle 1 - 100 times more sample. Packed columns require sophisticated interfacing devices for mass spectrometry and the analyst may lose 30% - 95% of the sample at the interface. Still another consideration is the peak width of the eluting compound - narrow peaks (generally the early eluting peaks) facilitate lower detection limits (higher sensitivities). With modern instruments, the use of capillary columns or SCOT columns in conjunction with chemical ionization and specific ion monitoring can produce maximum separating power and extreme sensitivity (nanograms or subnanograms of compounds per injection)(MC-166).

The use of a separate GC detector allows the analyst to obtain semiquantitative or quantitative information in conjunction with the qualitative analysis. The extent of the quantitative data depends on the separation achieved by the GC and the amount and degree of calibration of the instruments.

The auxiliary GC detector is not a necessity because the total ion monitor in a mass spectrometer acts in much the same fashion as a flame ionization detector. The response will often be proportional to the concentration when calibration is done by classes and internal standards are included in each run. Likewise, SIM detection with internal standards is proportional to concentration and will allow the operator to obtain semiquantitative information on compounds with coincident GC retention times. The reliability of the semiquantitative data is directly proportional to the concentration of the component being measured and the amount of time used to scan the peak.

The use of computerized spectral matching greatly facilitates the interpretation of GC-MS data. The value of this technique is greatly dependent on the algorithm used for the "matching" (CO-316) Thus, merely having a library of spectra to search and a search routine does not mean that all compounds for which a reference exists can be identified. A significant portion of interpretation time must still be devoted to examining the computer "matches."

Gas chromatography is a technique often used and misused for qualitative analysis. In order to be used properly, the instruments must be extensively calibrated for retention time measurements, the sample must be defined (i.e., light hydrocarbons, polynuclear aromatic hydrocarbons, fatty acid esters, etc.) and in many instances the use of selective dedectors is necessary. Every column (not every type of column) must have been calibrated. Definition of the sample may be accomplished by prior separations or selective derivatization. Selective detectors such as flame photometric for sulfur and phosphorous, Hall conductivity for nitrogen, sulfur or halogens, electron capture for electronegative compounds provide a degree of specificity based on more favorable response factors for some compounds than for others.

High pressure liquid chromatography generally has the same difficulty for qualitative analysis as GC. Its major advantage over GC is that the analyst can obtain separations of: very polar materials without derivatization; thermally labile compounds; and highly reactive compounds.

It must be stressed that HPLC is a relatively new technique but one of great importance in the analysis of very polar water soluble compounds. No commercial interfaces are yet available between this technique and mass spectrometry, but this combination is a logical one. A variety of approaches have been proposed (JO-148)(BA-353)(CA-251).

Paper and thin layer chromatography have limited utility in qualitative analysis but their separating power combined with the availability of specific visualization reagents make the two techniques useful on occasion. Most functional group spot tests which produce colored responses can be adapted as visualization reagents. In addition, fluorescence and fluorescence quenching provide general detection capabilities. Standards must be run with each set of unknowns. Their primary use on this problem is for analysis of polycyclic aromatic hydrocarbons (SA-184).

Fluorescence and ultraviolet spectrometry are also primarily of use in the analysis of polycyclic aromatic hydrocarbons. These materials will have distinctive excitation and emission spectra as well as distinctive ultraviolet absorption spectra. In some cases, these techniques may provide the only definitive qualitative information. These spectroscopic techniques begin to lose utility as the compounds become alkylated and are often combined with TLC which can effect separations and provide the Rf values as more data for identifications (TO-054). Fractions trapped from a GC eluent may be used in conjunction with either of the above techniques (SA-172). Standard spectra are required in all cases. Quantitative and qualitative analysis may be done simultaneously if prior calibrations have been made. The techniques are sensitive into the low submicrogram range.

Spark source mass spectrometry is perhaps the most sensitive and universal technique available for inorganic analysis (BR-240). With care, semiquantitative analysis is possible for most elements on a routine basis (HA-330). Matrix effects are important and a predominantly organic sample must be ashed before being analyzed. If certain metals predominate in the mixture, special calibrations may have to be made in order to do semiquantitative work.

The article by von Lehmden, et al (VO-027) demonstrates the applicability of SSMS to environmental samples and contrasts this to other techniques for inorganic analysis. This article also demonstrates that although the precision of the technique is often poor on an absolute basis, SSMS is as precise as other popular techniques.

Optical emission spectrometry is an acceptable alternative to SSMS. The technique is more widely available than SSMS but somewhat less sensitive. Sensitivities are on the order of tens of nanograms per run compared to tenths of nanograms for SSMS (BR-240). Optical emission is generally somewhat less costly than SSMS so the analyst must determine which is the most cost effective technique. The analyst should also be aware of which trace metals are of interest in the sample in order to choose the analytical technique.

X-ray fluorescence does not have the sensitivity of the two previous techniques. Detection limits are seldom below hundreds of nanograms. The primary advantage of XRF is that little or no sample pretreatment is required and that the technique is nondestructive. XRF is dependent on particle size and sample thickness.

Ion selective electrodes are not generally considered to be a qualitative analytical tool, however, when potential interferences are removed, the analyst can obtain qualitative and quantitative information simultaneously. The technique would be useful primary for anions. Sensitivity is in the range from tens to tenths of micrograms per unit volume.

1.6 Specific Applications at Level II

Not all of the above Level II techniques have been recommended for use in the specific examples in this report. Verification of the applicability of specific techniques is given below. No recommendation of the listed GC columns is intended, they are merely examples and not necessarily the best examples.

Streams from the Atmospheric Still

Light Ends. These are analyzed on-site as described in Section 1.1.4.

Naphtha Cut. The neutral organics fraction can be analyzed by GC-MS using a squalene capillary column (GA-132).

The acidic fraction can be analyzed by GC-MS. The GC separation of thiols has been accomplished using DC 550 (RA-175) and of phenols using Dexsil 300 (BU-159). It is suggested that both classes could be separated on Dexsil 300 or Dexsil 400.

The alkaline organic fraction can be separated on Triton X-305 (PO-133).

The very polar materials can be separated on Porapak QS (WA-188).

Distillate Cut. The nonpolar cut from CC on silica gel can be analyzed by GC-MS using squalene as cited above.

The moderately polar cut can be analyzed by GC-MS using an Apiezon L capillary column (CH-232). Most probably, the squalene column would also suffice for this fraction.

The polar cut from CC can probably be analyzed on Dexsil 300.

The acidic, basic, and polar fractions can be handled as cited for the naphtha cut.

It may, however, be advisable to methylate the acidic fraction in which case a polyester liquid phase would be appropriate.

Gas Oil Cut and Topped Crude. The various polynuclear aromatic fractions can be analyzed by GC-MS using an SE-52 capillary column (CA-241).

The various polar fractions obtained from reversed phase liquid chromatography can be analyzed by GC-MS. Suggested GC columns are Dexsil 300 or Apiezon L.

The acidic fraction should be methylated before analyzing the sample by GC-MS.

The other separations are as described above.

Concentrate from Atmospheric Still. The various fractions separated from the sample can be analyzed by GC-MS.

The nonpolar and moderatley polar cuts from the CC can be chromatographed on squalene as above.

The polar cut can be separated on a polyester column and possibly on Dexsil 300.

The conditions for the acidic, basic, and polar fractions are as for the naphtha cut.

Effluent from the API Separator. The GC-MS analyses here are essentially the same as for previous streams.

The TLC separation can be conducted according to Sawicki (SA-184).

The GC-MS analyses of the cuts from CC should perhaps be conducted using the conditions cited for Gas Oil.

Sulfur Recovery Unit Tail Gas. The various fractions can be analyzed with procedures described earlier.

Catalytic Cracker Regenerator Off Gas. The various fractions can be analyzed with procedures described earlier.

General Comment. The GC columns listed above are not the only columns which will effect the desired separations. No effort has been made to list all of the workable columns. In many cases the listed columns may not effect the desired separation because of the complexity of the mixture. In such a case the analyst has two choices: (1) to use several columns successively to separate as many compounds as possible, or (2) to use more front end separations (e.g., separate sulfides from aromatics (RA-175)) before using gas chromatography.

1.7 Level III Analyses

The primary difference between Level II and Level III analyses is the amount of calibration required. Those Level II techniques which are amenable to rapid and accurate quantitative work can be used in Level III.

Gas chromatography will be used more than GC-MS because once an effective separation has been achieved and as many compounds have been identified as are practical, there is no further need to use the high cost instrument.

Quantitative analysis using the specific ion monitoring capabilities of GC-MS may be necessary when GC separations are poor, however, the precision is not good, especially for trace quantities.

Level III analyses require that large numbers of calibration mixtures (solutions) be kept available. The purity of these standards must also be checked routinely.

Atomic absorption spectrometry (AA) is recommended for trace element analysis at Level III. There are, however, many instances where conventional AA techniques do not approach the sensitivity of SSMS. In these cases, modifications such as graphite furnaces or tantalum ribbon systems should be used. In other instances, flame photometry can provide the desired sensitivity.

1.8 Sensitivity and Detection Limits

Throughout this report there are references to sensitivities and to detection levels but these terms are meaningless unless considered in the proper context. For this reason, we will consider a methodology detection limit (MDL) which is meant to relate to the amount of a given compound which must be collected, separated from the matrix, and (an aliquot) delivered to the measurement device. This term departs from the normal concept of detectability and that is acknowledged. In this program, MDL is a function of sampling efficiency, sample integrity, efficiency of recovery during separation, degree of concentration and detectability limits (DL) of the measurement technique.

For purposes of illustration only, the following example is presented. The conditions are arbitrary assumptions.

1. Assume sampling efficiency equals .95,

2. Assume sample integrity factor of .95,

3. Assume extraction efficiency of .85,

4. Assume three liquid-liquid partitioning steps with .95 recovery in each step = .857,

5. Assume aliquot is 2% of total sample = .02

6. Assume factor of 5 over detectability level for good identification = .2, therefore

   $$\text{MDL} = \frac{1.0}{(.95)(.95)(.85)(.857)(.02)(.2)} = (420)\ \text{DL in grams.}$$

7. Assume detectability level of measurement as in list below.

This is an almost ideal situation, in reality the conditions could be:

#1 = .5

#2 = .7

#3 = .5

#4 = .6 at each of three steps = .216

#5 = .2% = .002

#6 = 25 (due to background interference) = .04, therefore

$$\text{MDL} = \frac{1}{.000003} \times \text{DL} = (333333)\ \text{DL in grams},$$

thus, a small change in each of the governing variables caused an 800 fold change in the effectiveness of the proposed methodology.

THE ANALYST MUST KEEP IN MIND THAT DETECTABILITY LIMITS OF A MEASUREMENT ARE ONLY A CONTRIBUTION TO THE ANALYTICAL LIMITATIONS OF THESE SCHEMES.

Other factors such as adsorption of trace materials, reactions during separations, high backgrounds, etc., can contribute another 2 - 3 orders of magnitude decrease in MDL.

Detectability limits for the various named measurement techniques are (KA-191):*

Gas Chromatography (FID)	10^{-11}g
Gas Chromatography (FPD)	10^{-11}g
Gas Chromatography (Hall)	10^{-9}g
Thin Layer Chromatography (color)	10^{-6}g
Thin Layer Chromatography (fluor)	10^{-9}g
Mass Spectrometry (electron impact)	10^{-12}g
Mass Spectrometry (chemical ion)	10^{-10}g
Mass Spectrometry (GC-MS)	10^{-11}g
Mass Spectrometry (spark source)	10^{-13}g
Atomic Absorption (flame)	10^{-6}g
Atomic Absorption (flameless)	10^{-9}g
Infrared (standard)	10^{-6}g
Infrared (Fourier transform)	10^{-9}g
X-Ray Fluorescence	10^{-7}g
Ion Selective Electrodes	10^{-15}g
Emission Spectrometry	10^{-9}g

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* The author of this report disagrees with many of these limits for real world samples using commonly available instrumentation.

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